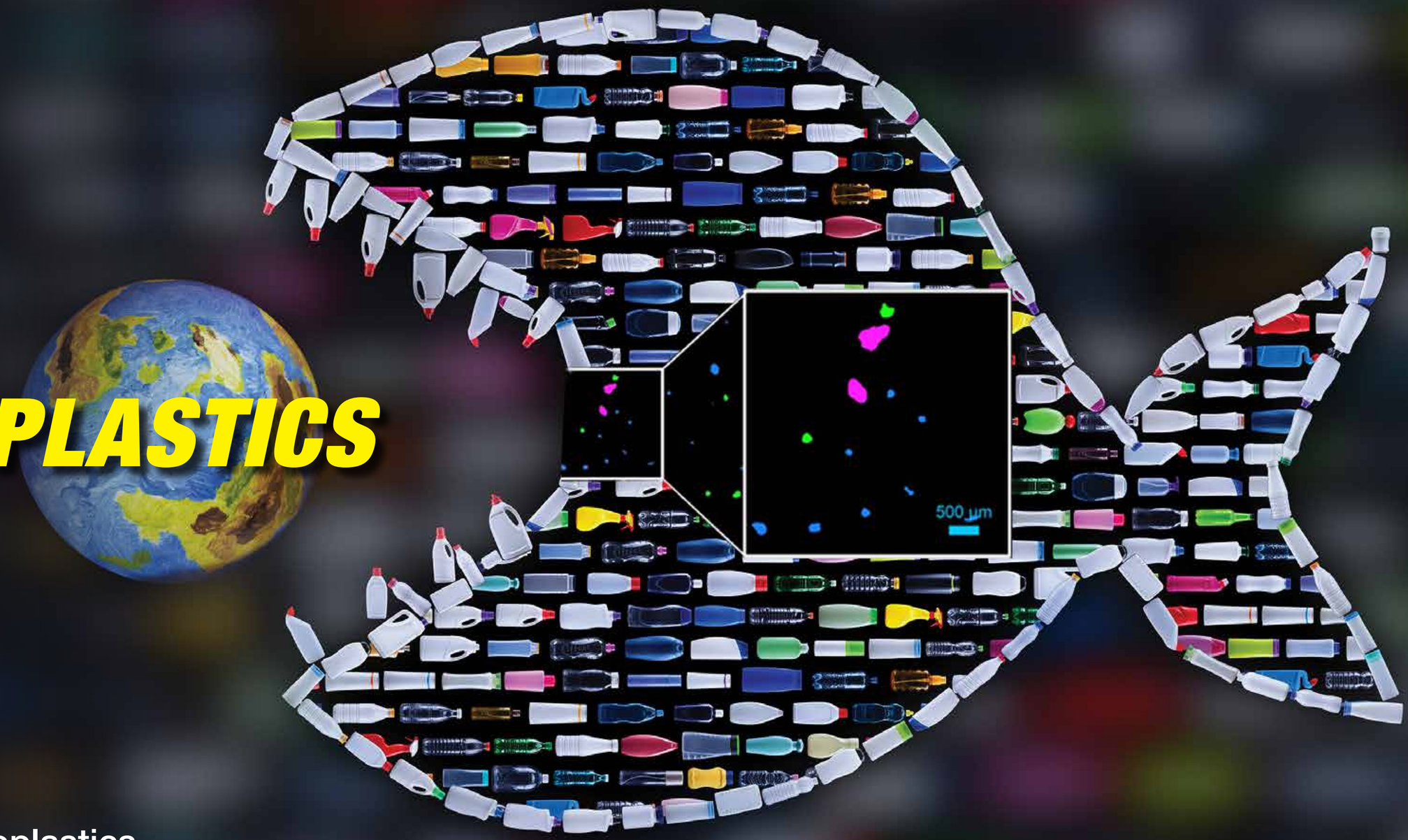
MICROPLASTICS



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What are microplastics?

Microplastics are small bits of plastic, 5 millimeters or less, and either engineered for end-products, or the result of environmental degradation of polymer-based trash.

Where do microplastics end up?

Advancements in manufacturing and our under-performing recycling habits have unintentionally created a new type of pollutant — microplastics —engineered or degraded polymer bits, 5 millimeters or smaller.

And although often hidden from view, they can threaten our ecosystem.

Researchers have found microplastics in marine and terrestrial life.They invade the food chain, and they've even been found in salt, sugar, beer, alcohol, and honey. Not to mention glaciers and rainwater.

Primary versus secondary microplastics

Primary microplastics are directly released into the environment as small plastic bits. These are intentionally engineered particles, like those found in some consumer and industrial products. Cosmetics, for example, have used microplastics as abrasives, and textiles use them for durability.

Secondary microplastics are the result of the degradation of large plastic waste, like plastic bags and bottles, into smaller plastic fragments when exposed to our environment.

Scientists use engineered microplastics in many areas, including cosmetics, personal care, detergents, paints/coatings/inks, industrial abrasives, agriculture, pharmaceuticals, wastewater treatment and construction. But these particles often weather, degrade or abrade from environmental or physical events, ending up in our oceans and elsewhere.

Why produce microplastics?

Manufacturers engineer primary microplastics because of the unique physical and chemical properties created by its small scale. Those properties include durability, rigidity and abrasiveness. Density, size, shape and composition influence their properties.

Microplastics from waste

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Where do microplastics end up, cont.

Microplastics in the oceans

About three quarters of all plastics that end up in the ocean originate on land, and are subsequently transported by rivers to the seas.

Plastic refuse, including discarded plastic bags and bottles, eventually breaks down into microplastic particles after being subjected to sunlight, sea water and the atmosphere. Marine life consumes these particles, mistaking it for food.

One the other hand, producers use engineered microplastics in a number of manufactured goods, including, abrasives, laundry detergent and tires. The abrasives and detergent wash down our sinks and migrate into our tributaries from wastewater and groundwater discharge, eventually finding their way to our oceans.

Microplastics in tires degrade from wear and spill onto our roads. Rain then carries it into our waterways.

Microplastics in water

Researchers have found microplastics in fresh water, wastewater, bottled water, and tap water.

Microplastic particles from plastic water bottles separate from the container and seep into the water we consume. Engineered microplastics from pollution, industrial and consumer goods get into our water supplies through runoff, consumption, and waste disposal with subsequent purification that cannot trap the tiny particles.

Microplastics in fish

Microplastics can act as carriers for toxic materials and harmful organisms, which often latch onto its surface. Fish consume microplastics, and become exposed to these substances, posing a threat to its health. Moreover, by eating microplastics instead of food, marine life may be deprived of the nutrients it needs to survive.

Microplastics in humans

We unwittingly consume roughly 5 grams of plastic each week in the form of microplastics, according to Australian researchers. That's like eating a credit card every seven days — or more than a half-pound of plastic in 12 months.

Studies suggest humans eat and inhale up to 74,000 microplastic particles a year. Those who drink only bottled water ingest an additional 90,000 particles annually.

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What are the health risks of microplastics?

Microplastics can be toxic, depending on its composition. It can also act as a carrier of other molecules that cling to it. Some of those clinging molecules are bacterial, viral or toxic.

Scientists fear the cumulative buildup of these toxins might affect the health of living organisms. Yet researchers are unsure about the volume of microplastics a body can tolerate, or the damage it may cause.

What we do know is this — consuming microplastics can physically damage organs and leech hazardous chemicals like pesticides. Scientists have shown that these substances can weaken immune function and hinder growth and reproduction.

The World Health Organization reported in 2019 that the current level of microplastics in drinking water doesn't pose a health risk – yet. But the group said we need to know more.

Researchers from Johns Hopkins looked at the impact of eating seafood contaminated with microplastics. Their conclusion? The accumulated plastic we take in could damage the immune system and upset a gut's balance.

Still, the research on health effects are slim. Recent studies, through particle analysis and Raman spectroscopy, have begun to identify various microplastic types. Scientists are developing sampling, extraction and analysis methods so we can trace these particles back to their sources. That way, we can create public policy to address this potential threat.

Where do microplastics come from?

Enjoying your crisp new white shirt? Or that Sunday drive? Good.

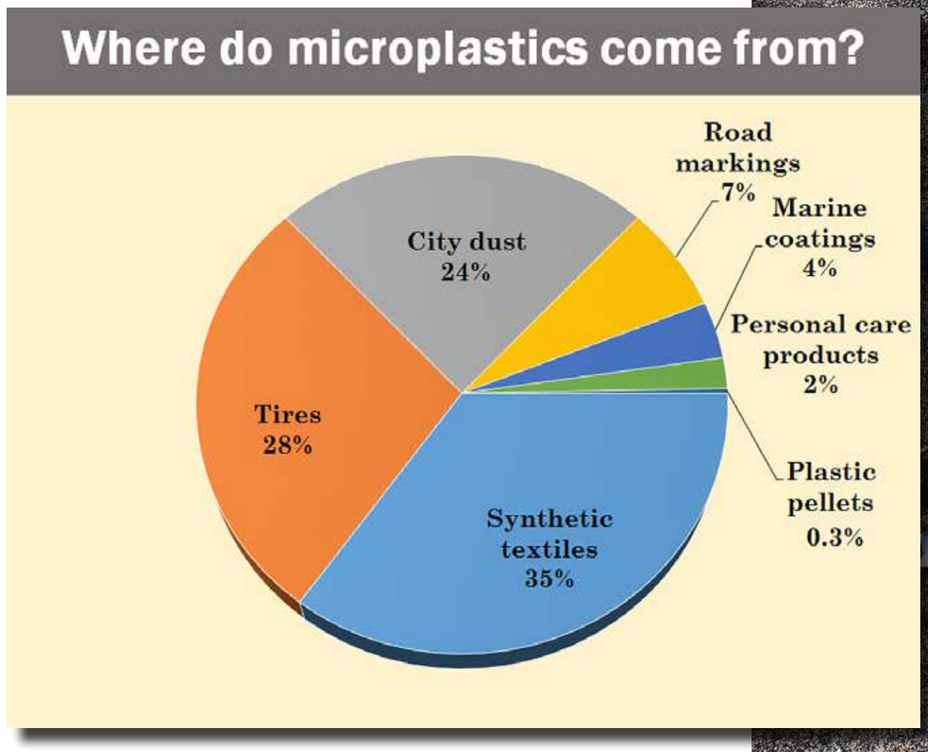
But consider that these 21st century essentials may be among the largest contributors to a new environmental hazard.

Microplastics — tiny plastic particles smaller than 5 mm – can come from things like that shirt or those car tires and seep into our biosphere. Microplastics also come from plastic trash. The sun, air and sea break down dumped plastic waste into smaller, microplastic particles, which also enter our environment.

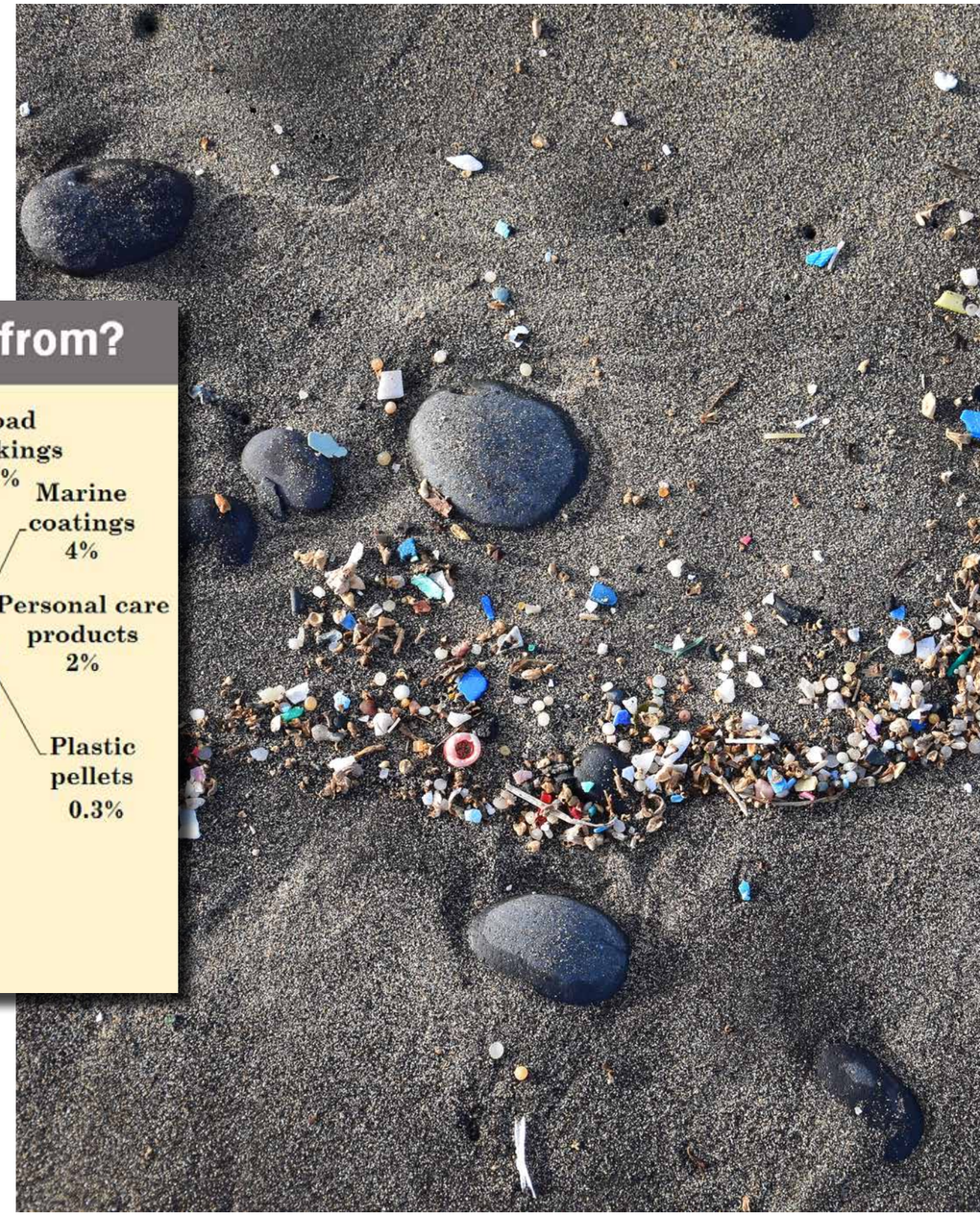
Manufactured microbeads, used especially in cleansing products as exfoliating agents and in manufacturing processes, are also part of the problem.

These tiny bits of plastic find their way into our aquatic systems, which are ultimately ingested by sea life. Humans consume, inhale and absorb these particles through our skin.

A study by the International Union for Conservation of Nature (IUCN) found that ordinary consumer products are the source of most of the ocean's primary microplastics.



Source: International Union for Conservation of Nature, 2017



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Where do microplastics come from? - cont.

Here's an explanation of those sources.

Synthetic textiles

Synthetic textiles are the single greatest contributors to engineered microplastics in the ocean, accounting for 35 percent of the total volume.

Polyester, nylon, acrylic, and other synthetic fibers – each a form of plastic – make up 60 percent of the fabric content of our clothes. Why? Synthetic microplastic fibers are cheap and versatile. The fibers create stretch, allow breathability in activewear, and warmth and sturdiness in winter clothes.

But washing synthetic textiles frees engineered microplastics through abrasion and shedding of fibers from the fabrics. That's due to the mechanical and chemical stresses that fabrics undergo during a washing process in a laundry machine.

Your plumbing sends the spent water from your washing machine to a wastewater treatment plant. These fibers, too small for the plant to filter, are discharged with treated wastewater. The fibers eventually find their way to the oceans.

Natural fabrics like cotton shed, too. But while many natural fibers biodegrade, synthetics don't.

Tires

Things were so much simpler when tires were made of wood.

Today, about 24 percent of a tire consists of synthetic rubber, a plastic polymer, and 19 percent natural rubber. Microplastics form a matrix of the synthetic polymers, giving the tire both rigidity and traction. The rest of the tire is metal and other compounds.

Tires erode through heat and friction from contact with the road. The wind and rain spread the tire dust and wash it off the road. It enters tributaries, lakes and eventually, the oceans.

A Canadian study found that passenger light truck tires lost nearly 2.5 pounds of rubber during an average service life of just over 6 years. Another study found that Americans produce the most tire wear per capita and estimated that tires in the U.S. alone produce about 1.8 million tons of microplastics annually.

Second only to synthetic textiles, vehicle tires contribute 28 percent of all the primary microplastics in the oceans, according to the IUCN.

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Where do microplastics come from? - cont.

City Dust

City dust, which accounts for 24 percent of microplastics in the oceans, comes from a variety of sources. While each is a small contributor, it adds up in a populated area.

Weathering, abrasion and detergents create city dust from manmade products.

City dust includes losses from the abrasion of objects like synthetic soles of footwear and synthetic cooking utensils, of infrastructure like household dust, artificial turfs, boats, and building coatings from harbors and marinas. It also includes particles from the blasting of abrasives, weathering of plastic materials and use of detergents.

Scientists recorded 365 microplastic particles per square meter falling daily from the sky in the Pyrenees Mountains in southern France. That was 60 miles from the nearest city. The authors of the 2019 study called microplastics a “new atmospheric pollutant.”

Road Markings

Crews apply road markings while building and maintaining roadways. The substances used include polymer tape and paint. Thermoplastics which become soft and flexible at warmer temperatures are popular in Europe.

Microplastics may result from weathering or abrasion by vehicles. The materials are either spread by wind or washed off the roads by rain before reaching surface waters and potentially the oceans.

Debris from road markings make up about 7 percent of the primary microplastics in the ocean.

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Where do microplastics come from? - cont.

Marine coatings

Operators apply marine coatings to all parts of seagoing vessels for protection. These includes the hull, the superstructure and on-deck equipment. The materials involve solid coatings, anticorrosive paint or antifouling paint.

Developers use several types of plastics for marine coatings, including mostly polyurethane and epoxy coatings, vinyl and lacquers. Weathering and spills during application, maintenance and disposal of these coatings cause the release of primary microplastics.

Marine coatings account for 4 percent of primary microplastics in the ocean.

Personal care products

Many personal care and cosmetic products contain a type of engineered microplastic known as microbeads. The products include scrubbing agents, shower gels and creams.

The U.S. government banned its manufacture and sale, but producers still make and sell these products globally.

Microbeads are manufactured polyethylene plastic. They act as an exfoliant, delivers active ingredients, and controls viscosity in health and beauty products.

Plastics make up as much as 10 percent of some personal care products' weights. That's more than the packaging material. Some items have several thousand microbeads per gram of product.

Once the personal care item is used, it ends up in wastewater. These tiny particles easily pass through water filtration systems and end up in our waterways.

Personal care products and cosmetics represent 2 percent of all primary microplastics in the oceans.

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Where do microplastics come from? - cont.

Plastic pellets / Nurdles

Manufacturers produce several plastics in the shape of small pellets or powders, the primary form of plastic. These producers then transport the pellets to plastic transformers that make end products. Pellets can inadvertently spill into the environment during manufacturing, processing, transport and recycling. Plastic pellets make up 0.3 percent of the ocean's primary microplastics.

In 2019, the state of Texas fined a New Jersey-headquartered Texas plastic manufacturer more than $120,000 after spilling thousands lentil-sized plastic pellets or "nurdles" into a creek and bay on the Gulf Coast. The company spilled the nurdles near its 2,500-acre Texas complex, about halfway between Houston and Corpus Christi.

Nurdles can also degrade into microplastics.

Texas required the company to recover and properly dispose of about 439,000 pounds of debris and plastic from the waterways.

Nurdles can absorb dangerous industrial and consumer chemicals including insecticides, PCBs and mercury. The pellets can clog the digestive systems of marine animals if ingested for food, and eventually cause them to starve to death. Nurdles can also degrade into microplastics.

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Microplastics pose a tough road ahead

Waste management and personal usage of plastic products can help address the volume of secondary microplastics in the oceans. But the problem with primary microplastics is more complicated.

Primary microplastics can improve the performance of consumer and industrial products. It has a positive economic effect, and improves our safety, comfort and standard of living. These products are ingrained in our economy, technology, and way of life.

The lack of clear and overwhelming data showing that microplastics are harmful to humans makes it tough to legislate changes in its industrial usage.

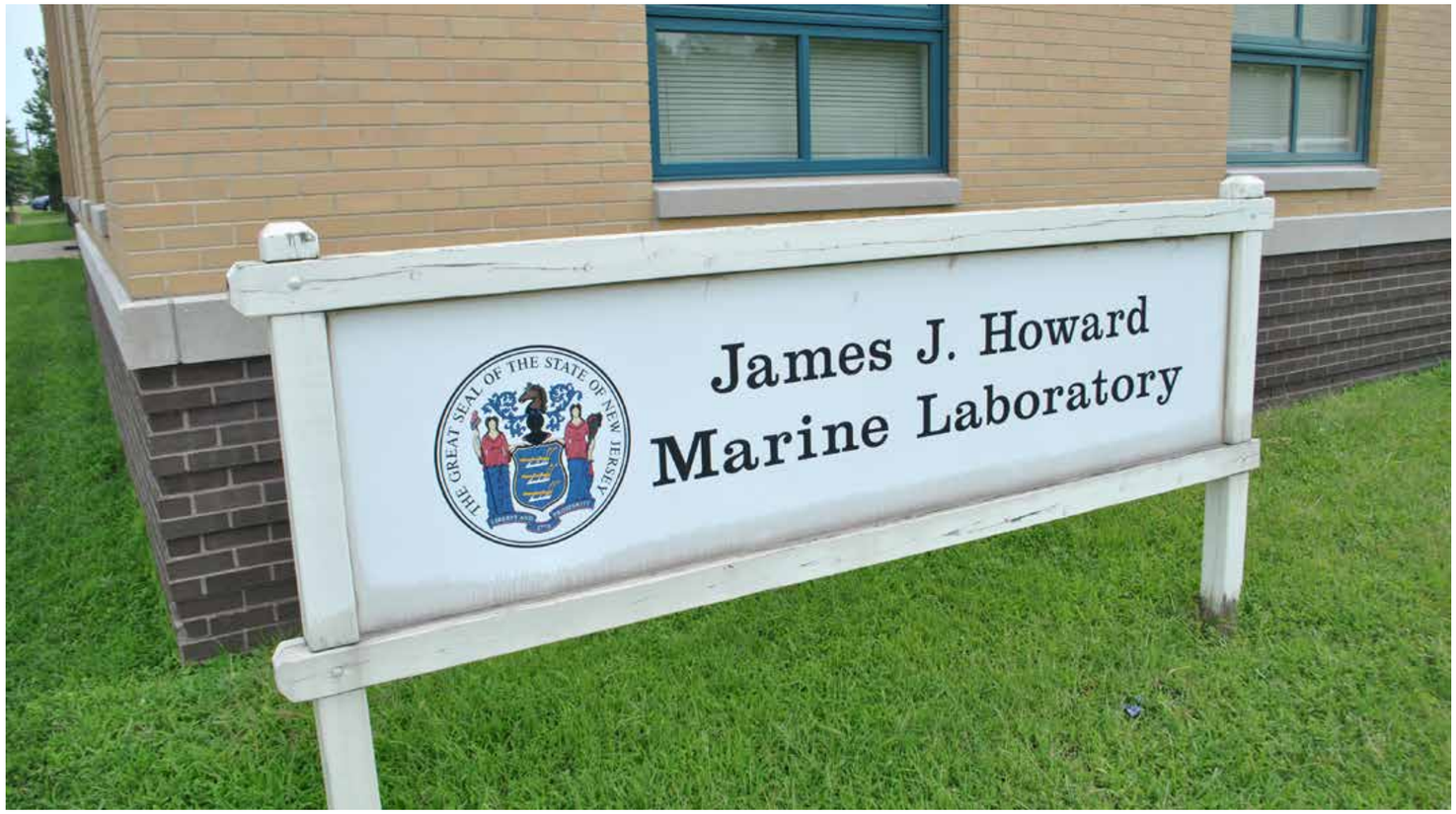
However, the U.S. Congress did pass the Microbead-Free Waters Act of 2015. It banned the manufacture and retail sale of microbead-containing personal care products. All provisions of the act went into effect by 2018.

More conclusive research into the health effects of microplastics may be a prerequisite for greater regulatory change. That and a legislative environment receptive to limiting the impact of primary microplastics on our environment.

Stories

According to various estimates in 2016, between 15 and 51 trillion pieces of microplastics are in the world's oceans.

Characterizing microplastics



That fancy iced coffee you downed this morning might give you more than a jolt. A common accessory - the plastic straw - is contributing to a type of contaminant affecting our ecosystems, not to mention the human food chain.

The pollutants are called microplastics, tiny bits of plastic that break down from larger pieces and are ingested by sea life. And eventually by humans. Microbeads are also part of the problem. These are extremely small pieces of engineered plastic, used especially in cleansing products as exfoliating agents. The detection of microplastics has become an important research goal.

But why straws? They are small and often bypass recycling automation. If it doesn't go to landfill, it can end up in our oceans and lakes.

While some cities have taken to banning straws, others have considered banning other single-use plastic products, such as plastic water bottles, cutlery, and bags. It's the life cycle of these materials that can make them harmful.

About one million plastic water bottles were bought every minute across the globe in 2017, according to Forbes Magazine. Yet only nine percent recycled.

The rest end up in landfills, or on our beaches and in our parks. Some of those materials can wash away into our oceans, lakes, or rivers.

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Characterizing microplastics, cont.

What are microplastics?

Sand samples containing microplastics are prepared for analysis

When plastics are subjected to the sun, air and sea, the larger pieces fragment or degrade into smaller pieces. The smallest pieces, with a size of smaller than 5 millimeters, are called microplastics. Some are microscopic and pass through filters meant to remove impurities from our drinking water.

Researchers ran tests on 259 bottles of water from 11 brands bought in nine countries, according to Time Magazine. More than 90 percent of the examined bottles contained microplastics.

Different plastic types have different toxicities, according to Ashok Deshpande, Ph.D., a research chemist with the Northeast Fisheries Science Center of National Oceanic and Atmospheric Administration (NOAA) in Sandy Hook, New Jersey.

And different polymers accumulate various contaminants to different extents. Plastics also accumulate bacteria, viruses, chemicals and harmful algae.

“The plastics act as a conduit for the transport of the algae and colonizing bacteria,” Deshpande said. Microplastics can be mistaken for prey by fish. Fish think it’s their food – the aquatic life can’t distinguish between microplastics and food. The microplastics affect the fish when they are ingesting it, mostly choking up the fish’s digestive system. The fish thinks it’s not hungry. So it starves to death. Since plastics are the conduits for chemical contamination, the fish can be subject to all those agents too.

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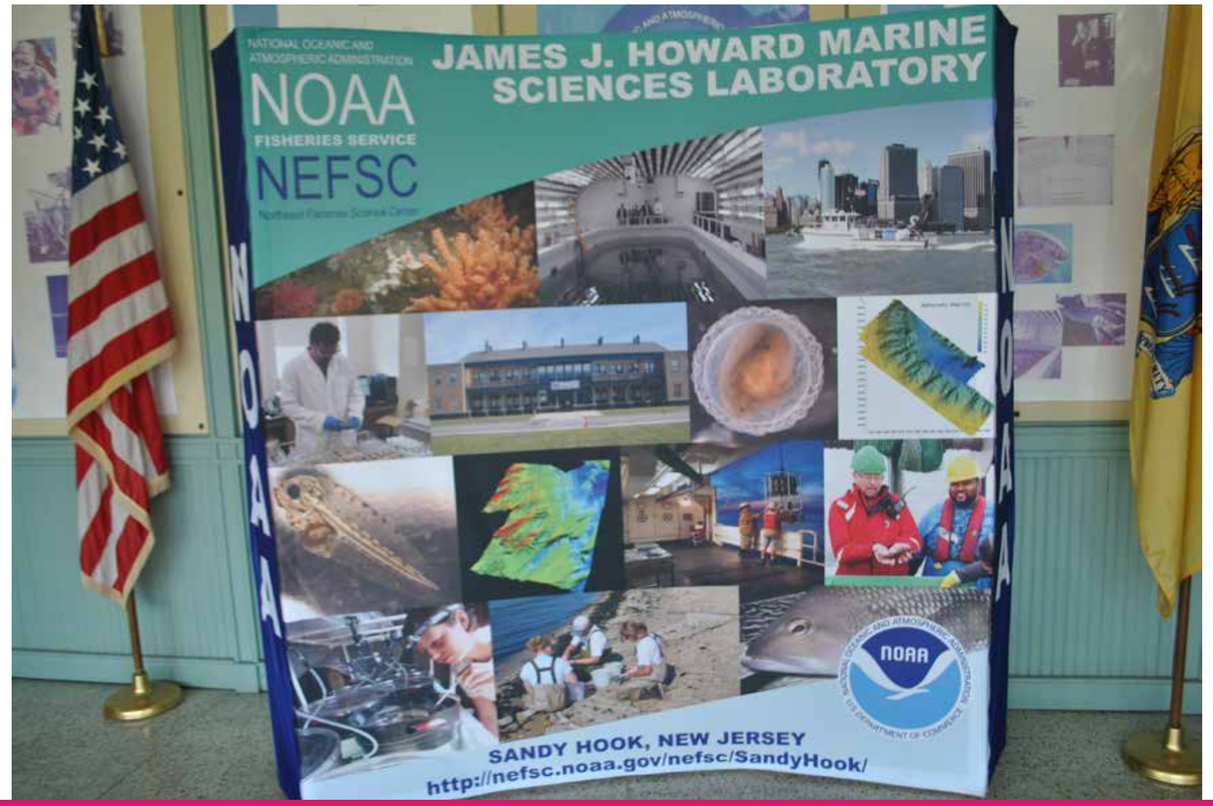
And people, of course, eat fish.

According to a study Deshpande was involved in 15 years ago, the contaminants in the fish off Sandy Hook tested within U.S. Food and Drug Administration’s acceptable levels. But that was 15 years ago.

“We are just beginning to do the research on the fish,” he said. “Different studies have shown how the plastics affect the fish and shellfish. These are ongoing and there are no conclusions now. But if they eat microplastics, it’s definitely not good for them.“

The World Economic Forum warns that there will be more plastics in the ocean by 2050 than fish.



Characterizing microplastics, cont.

The science of microplastics

To characterize the microplastics found in fish, multiple technologies can be applied, such as gas chromatography (GC) pyrolysis, mass spectrometry, infrared (IR) spectroscopy, or Raman spectroscopy, according to Deshpande. Raman microscopy combines Raman spectroscopy and optical microscopy, and is one of the most efficient and effective ways to identify polymers. It allows the researcher to analyze microscopic pieces of plastics by focusing the laser beam to a tiny spot, and obtaining Raman spectra from it. Raman spectra are characteristic to each polymer, and can be identified by searching the library of known polymer spectra.

Chelsea Rochman, Ph.D., Professor at University of Toronto's Department of Ecology and Evolutionary Biology, uses a Raman microscope to study microplastics. She tries to understand how much microplastics exist, their size, and what they are. There are so many different types of plastics out there, she pointed out, that analytical tools, like Raman, are necessary to characterize these materials, which help gauge their impact on animals.

Her group is pursuing faster and more accurate ways to analyze microplastic samples. The goal is to increase the efficiency of the analytical methods to answer relevant questions more effectively. It's important to identify the type of polymers (or microplastics) because it can lead to identifying the source of the pollutants to the environment. This will, in turn, help to reduce contamination in the environment via social campaigns, consumer movements or regulatory actions. Rochman's group uses HORIBA Scientific's **XploRA™ PLUS Raman microscope**, and is developing sample characterization methods that are fast, easy, robust and accurate.

Deshpande said one of the next challenges is to identify the small fibers in shellfish and other small organisms. He said shellfish "ingest microplastics, and fish eat thousands of them, as well as zooplankton. Imagine how much fish are ingesting. The bigger fish have double exposure because they can eat smaller sea life and bigger pieces of plastics."

Ashok Despande Ph.D., a research chemist with the Northeast Fisheries Science Center of National Oceanic and Atmospheric Administration (NOAA) in Sandy Hook, New Jersey

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The rapid analysis of large number of collected particles allows for an exhaustive assessment of both large sample sizes and small subsamples.

Morphological and chemical characterizations of microplastic particles using ParticleFinder™ and Raman techniques

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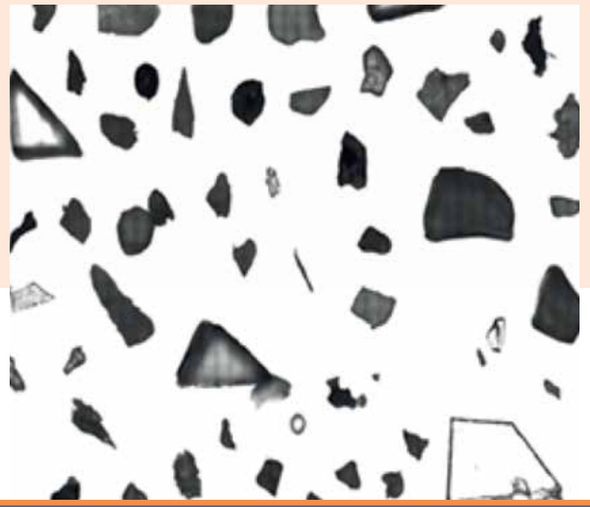

Abstract: The assessment of microplastics in a marine environment is a multi-step process (sampling, extraction, detection and quantification of microplastics), in which each step is time consuming. Analyzing the chemical composition and morphology of microplastics represents a real challenge for answering crucial questions about the sources and fate of microplastics in aquatic environments. In this application note, we present a reproducible and time-effective method for fast and thorough morphological and chemical characterization of microplastics using semi-automated scanning of particles coupled to micro-Raman spectroscopy. The rapid analysis of a large number of collected particles allows for an exhaustive assessment of both large sample sizes and small subsamples.

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Morphological and chemical characterizations of microplastic particles using ParticleFinder™ and Raman techniques, cont.

Introduction

The scientific community is increasingly interested in environmental contamination by plastics. Recently, this interest in the contamination of aquatic systems by plastics has shifted to smaller particles, microplastics. Microplastics are plastic particles smaller than 5mm which can be directly made of microparticles, or are the result of the fragmentation of macroplastics. It has been shown that microplastics are the dominant size class among the debris of 92% of the 5.25 billion plastic particles that contaminate the ocean surface.

These plastic particles may contain potentially toxic additives to organisms (phthalates, bisphenol A, brominated flame retardants, nonylphenols, and antioxidants) which are incorporated into the polymers during their design in order to extend their life, giving them a better resistance to heat, oxidation and degradation mechanisms.

Given their harmful effects in the medium and long term, it is relevant to question and understand how they are fragmented, transported and dispersed in the marine environment. For this, it is essential to be able to characterize them morphologically and chemically.

The classical methodologies applied on large environmental samples are mainly based on visual sorting and characterization, and usually they are not sufficient.

In this application note, we propose an efficient methodology for molecular identification and morphological description of microplastic particles. The advantage of this semi-automatic method is the coupling between a Raman micro-spectrometer and image processing software, ParticleFinder™, within the same analysis in order to obtain physical (morphological) and chemical (molecular composition) information from particles.

Several hundred particles may be analyzed while minimizing the intervention of the operator (suitable for potential contamination or loss of sample) as well as agent time.

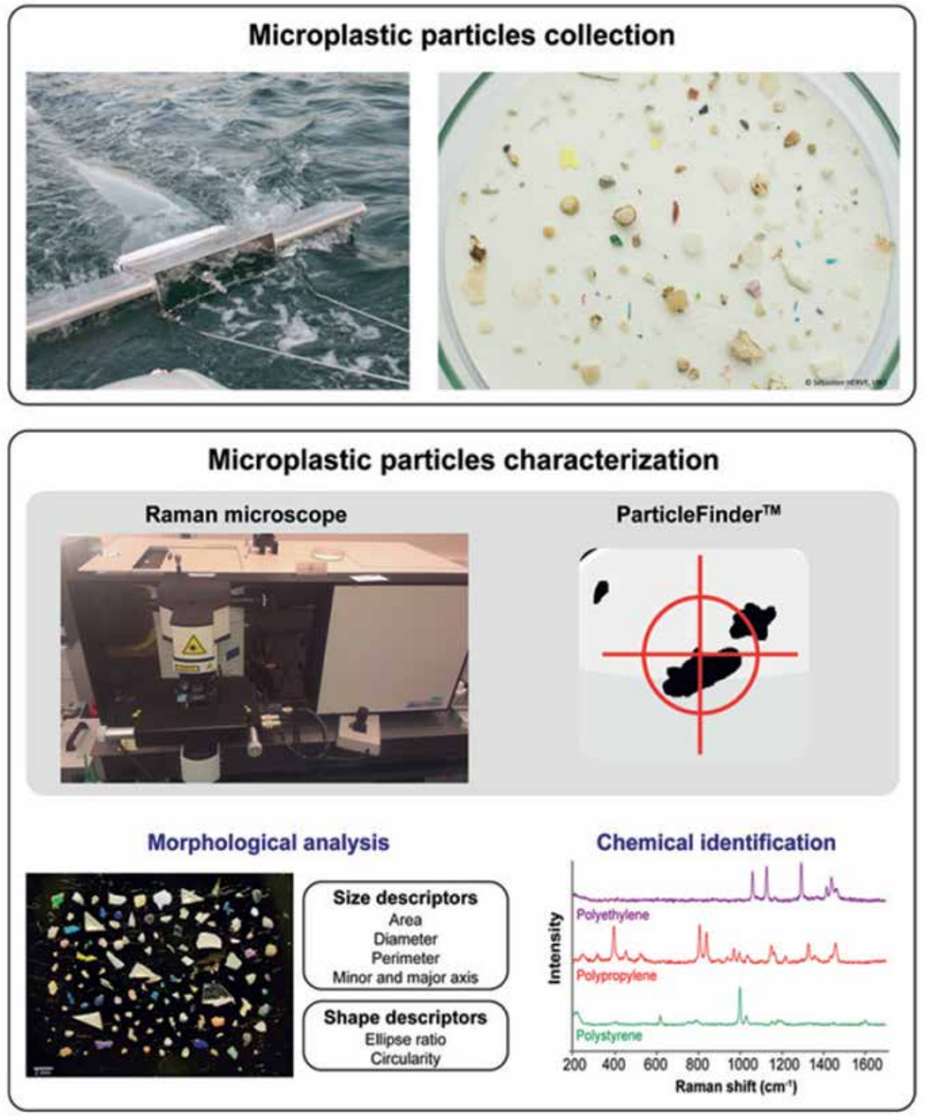

Figure 1: Typical workflow for the semi-automatic Raman micro-spectroscopy method for morphological and chemical characterizations of microplastic litter.

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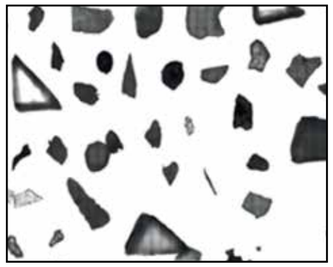
Morphological and chemical characterizations of microplastic particles using ParticleFinder™ and Raman techniques, cont.

Methodology

For the validation of the method, the study reveals the analysis of 103 particles randomly selected from floating micro-particles collected in the Bay of Brest (Brittany, France) in September 2014 using a Manta trawl. Particles of seven additive-free reference polymers were used as references and were positioned among 103 collected particles: polyethylene (PE), polypropylene (PP), polystyrene (PS), unplasticized polyvinyl chloride (PVC), polyethylene terephthalate (PET), polyamide-6 (PA-6) and polyurethane (PUR).

Raman analysis

Localization, counting, 2D morphological characterization and Raman measurements of the 110 (103 + 7) particles were carried out using a LabRAM™ HR800 Raman micro-spectrometer equipped with the ParticleFinder™ application for LabSpec 6. The particles were placed on a gold coated microscope slide, in order to avoid the Raman signals generated by borosilicate glass or "unclean" non-gold microscope slides. The image of a large area on the sample (25 x 21 mm^2) was captured and then used in ParticleFinder™ for further analysis in Figure 2.



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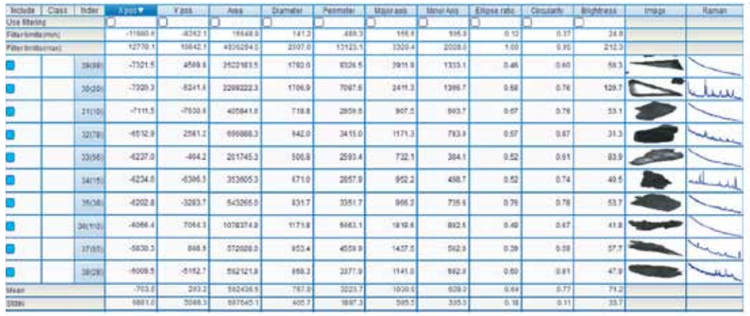

Figure 2b: Morphological analysis of microplastic particles of the 110 particles analyzed for method validation: Statistic of the 2D descriptors for each particle.

Statistics of key 2D morphological features (minor and major size, particle area, diameter, and perimeter) and 2D shape descriptors (ellipse ratio and circularity) were calculated by the software for each particle.

The next step cconsisted of the ParticleFinder software application performing the automatic motorized stage positioning and analysis of particles. One spectrum was collected on the center of each particle. Raman measurements were performed using 10-fold magnification objective (Olympus) and 785nm laser as the excitation line. The chemical identification of almost all particles was realized using commercial Raman libraries (KnowItAll™ Informatics Systems, Wiley®, Raman ID Expert). The measurements were repeated 3 times in 3 different runs under the same conditions, except for particle spatial location.

Once validated, the previously presented method was applied to a larger environmental sample (n=962 particles). Out of the 962 particles collected in surface water, 75% were chemically characterized. Microplastics (PE 48%, PP 12%, PS 11%) represented 71% of the whole sample (Figure 3). The 4% of identified particles remaining are quartz (2%) and carbonates (2%). The non-identified particles (25%) exhibited only PB15 dye spectrum (3%), spectra with no correspondence with databases (6%), or a signal that was either absent or saturated (16%).

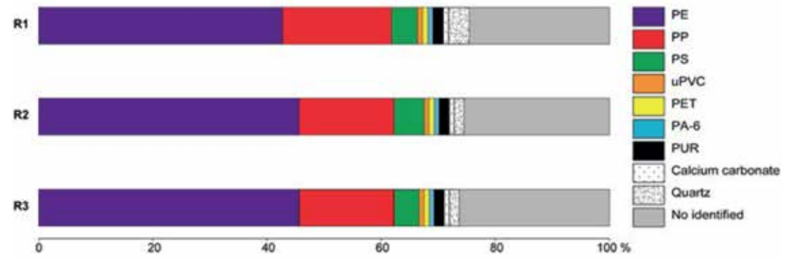

Figure 3: Proportion of each polymer family for 3 independent measurements.

Morphological analysis was based on descriptors as minor and major axis, perimeter, diameter, area, ratio ellipse and circularity. Significant differences were observed in the distribution of quartz, PE, PP and PS particles (Figure 4).

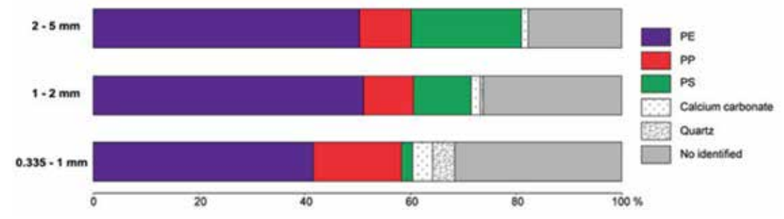

Figure 4: Proportion of particles identified, and not identified, in seawater samples (n=962 collected particles) depending on size class (0.333-1/ 1-2/ 2-5mm).

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Morphological and chemical characterizations of microplastic particles using ParticleFinder™ and Raman techniques, cont.

Conclusion

Every step of microplastic analysis (collection, extraction and characterization) is time consuming, representing an obstacle to the implementation of large scale monitoring. In this application note, we describe a semi-automated Raman micro-spectroscopy method, coupled to static image analysis, that allows the screening of a large quantity of microplastics in a time-effective way with minimal machine operator intervention. With this method, the complete analysis (Raman measurements and morphology descriptors) of a hundred particles takes around three hours for machine time and around 1 hour for machine operator intervention (without spectra identification).

The ParticleFinder™ module offers the possibility to accurately analyze the morphological features of all micro-particles (size, shape, density). Coupling it with powerful Raman capabilities for chemical identification, we provide a very efficient tool for environmental microplastic characterization.

LabRAM HR

Acknowledgements

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Frère Laura, Paul-Pont Ika, Moreau, Jonathan, Soudant Philippe, Lambert Christophe, Huvet Arnaud, Rinnert Emmanuel, 2016. A semi-automated Raman micro-spectroscopy method for morphological and chemical characterizations of microplastic litter. Marine Pollution Bulletin. Volume 113, Issues 1–2, pages 461-468.

https://doi.org/10.1016/j.marpolbul.2016.10.051
http://archimer.ifremer.fr/doc/00357/46802/46976.pdf

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Laboratory-based research must be performed to understand the capacity of microplastics to effect human and environmental health.

Understanding the nature of microplastic pollution and identifying environmental impacts

With the large-scale production of consumer plastics, comes the problem of how to deal with the disposal of long-lived single use items. Only a small percentage of plastics are recycled, leaving a significant volume accumulating in landfills or polluting our environment, where they fragment into smaller pieces, termed microplastics. Microplastics are ubiquitous and are present in every part of the environment and in the tissue of organisms, where they have physical and chemical toxic effects. To understand the extent of the problem, it is important to formulate standard methods for the collection, extraction, and identification of microplastics. In addition, laboratory-based research must be performed to understand the capacity of microplastics to effect human and environmental health. This review paper summarizes some of the key research direction in this field, in particular with respect to the research laboratories of Dr. Chelsea Rochman at the University of Toronto, one of the world's leading authorities on microplastic analysis and understanding of environmental and health impacts and risks.

Starting in the mid-twentieth century, plastics began to replace other materials, since they were easy and inexpensive to manufacture, while still being strong and durable. With the advent of plastics, came the idea of "throwaway living": the idea that consumers could save time through single-use items, including tableware and flatware, beverage and food containers, and diapers.[1] With the increase in manufacturing of disposable consumer products, the production of plastics has ballooned since 1950, with an estimated 8,300 million metric tons produced as of 2015. Of that amount, only 30% of manufactured plastics are still in use, while approximately 60% have been discarded and 10% have been incinerated.[2] The same characteristics that make plastics excellent materials for a wide variety of consumer uses, also make managing their disposal difficult. Lifetimes of plastics can range from tens of years to hundreds of years depending on the nature of the material.[3] Depending on the implementation of waste management standards, plastic waste may be landfilled, incinerated, recycled, or dumped into the environment. Evidence of plastic pollution has been well documented from the Great Pacific Garbage Patch[4] to "pristine" beaches littered with plastic trash.[5]

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Plastic litter comprises a wide variety of materials and sizes, including microplastics, particles less than 5 mm in size.[6] Sources of microplastics can be both primary and secondary. Primary sources include pellets from plastic processing plants, microbeads from cosmetic and personal care products, and industrial abrasives. Secondary sources of microplastics arise from the fragmentation and degradation of larger plastics. Examples include microfibers released from textiles and tire wear particles (see Figure 1).[7] Microplastics encompass a wide variety of characteristics. Their morphologies include fibers, films, fragments, pellets, foams, and spheres.[8] Microplastics also incorporate a wide variety of polymers including polyethylene (PE), polyethylene terephthalate (PET), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), and rubber. Microplastics are also not composed of polymers alone, but may also contain pigments or dyes and additives, such as titanium dioxide and calcium carbonate. The transport of microplastics to the environment can occur through a variety of mechanisms, including through air and water, for example, from laundering effluent and exhaust.[9] Sinks of microplastics in the environment include sediment, freshwater bodies (lakes, rivers), and saltwater bodies (surface water, arctic ice).[10] They can also be transported between organisms, for example from prey to predator, via trophic transfer.[11] Microplastics have been found in nearly every level of the food chain from invertebrates[12] all the way up to the largest mammals on earth.[13]

There is ample evidence in the literature that microplastics are harmful. Toxicity can take on two forms; Physical and chemical. Physical toxicity arises from the accumulation of microplastics in organisms and can have a variety of effects on health, including reduced respiratory function, hepatic stress, and the formation of granulomas through immune response.[14] As microplastics continue to break down into smaller and smaller fragments down to the nanoscale, translocation from the gut can occur leading to harmful effects in other tissues including the heart, lungs, gall bladder, and liver.[15] Chemical toxicity can arise from either additives in the plastics themselves or through the accumulation of toxins like persistent organic pollutants (POPs) or metals on the surface of microplastic particles.[14]

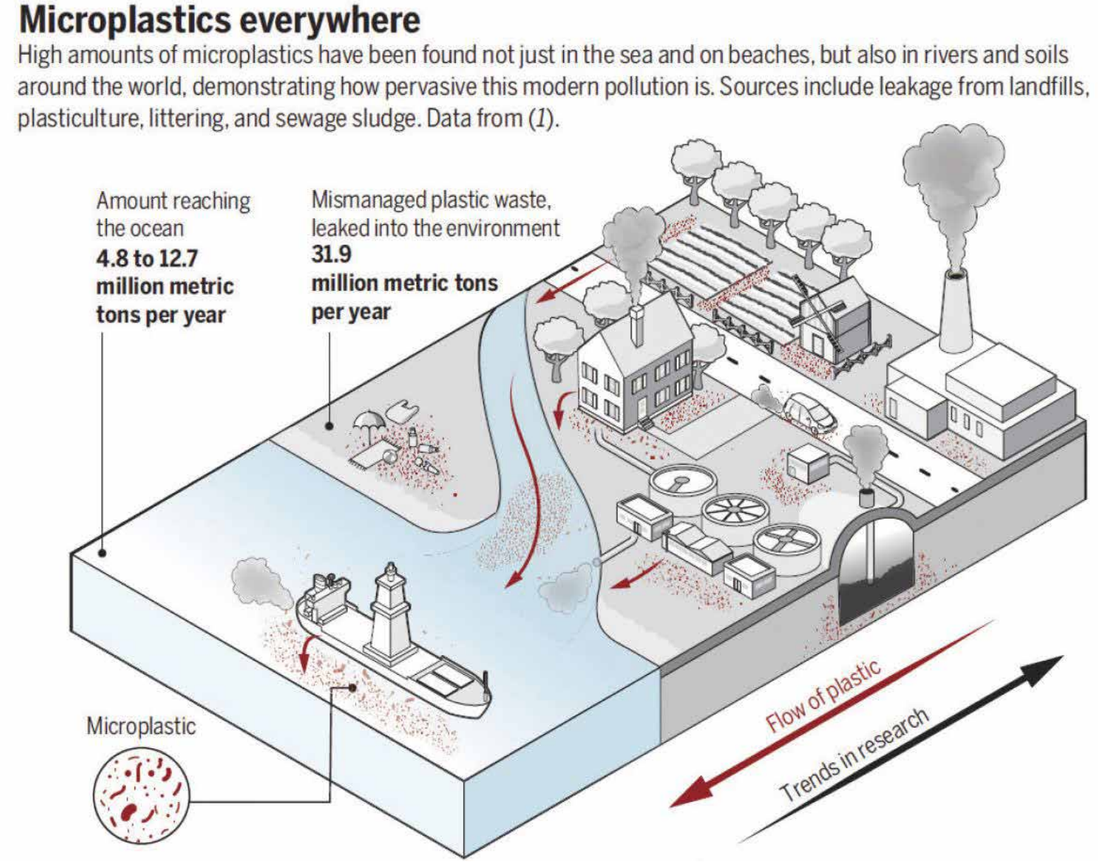

Figure 1: Reprinted with permission from Science Magazine (doi: 10.1126/science.aar7734).

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Critical to understanding the source of microplastics and potential toxicity is first understanding the presence and characteristics of microplastics in our environment. This includes elucidating the distribution of polymer types, presence of additives, particle morphology, and size distribution. In order to develop a clear picture, methods for collection, extraction, and identification of microplastics must be developed and standardized (or at least harmonized) for data synthesis.

Collection Methods

The most common method for the collection of microplastics from marine environments is the neuston net or Manta Trawl. Using this technique, a large volume of surface water can be sampled by towing the net via a boat. Designed for collecting plankton, the net's mesh size is generally in the range of 333-335 µm, so the size of microplastics collected is restricted to those in the larger size range. However, microfibers, which are thought to be one of the most prevalent microplastic morphologies, can slip easily through a net, in addition to any other particulate with ellipsoidal shapes (thin fragments or folded/rolled films). Finally, the material of the net itself may contribute to contamination in collected samples.[16]

Another method for collection from marine environments is the grab method. In this method, a 1 L (or larger volume) sample of water is collected, typically in a glass or metal sample container, to avoid contamination. Although the total volume is less than a net, a grab sample can collect plastics down to the sub-micron scale. In addition, because of the simplicity of collection, researchers of any skill level can easily collect samples, including citizen scientists. Samples may also be collected from a variety of environments including shallow tidal pools and wastewater outflow sites.[17]

Sediment samples require alternate collection methods - these include collection from coastal beaches to the deep sea. For sediment samples collected from the seabed, specialized equipment is required. These can include grab samplers which scoop a sample from the top layer of the sea floor (Van Veen, Ekman) and core samplers, which collect columns of sediment, retaining information on the numbers of microplastics in sediment as a function of depth. As in the case of nets, contamination from plastic core samplers is also a concern. Metal is an alternate choice, however the opacity of metal precludes the ability of the researcher to actively monitor the volume of sediment collected.[18]

Other common matrices include biota, which consists of sampling animals from the environment to bring back to the lab for processing. In addition, air samples are also becoming more common and methods for collection continue to be developed to capture both wet and dry deposition.

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Extraction Methods

During the collection of microplastic samples, particulate of other types may also be present including minerals, plant matter, biota, and other organic matter. There are a number of methods used to isolate microplastics of interest from other particulate, including density separation and chemical digestion. Density separation is used to separate denser particulate (e.g., minerals, silica) from the more buoyant microplastics. In density separation, the mixed sample matrix is immersed in a prepared solution with high density. Those particles with lower density than the solution, including microplastics, float to the surface, while heavier particles sink to the bottom. The solution is allowed to rest for an extended period so that the denser particles have time to settle before carefully extracting the top portion of the sample containing 'floating' particles. This process may then be repeated, through the addition of fresh solution to the settled portion of the sample to ensure that all microplastics are collected. Different solutions with varying density can be prepared including sodium chloride, zinc chloride, calcium chloride, and sodium iodide.[16]

A unique extraction procedure taking advantage of the hydrophobic nature of microplastics was developed and reported by the Rochman Lab at the University of Toronto. In this procedure, magnetic iron nanoparticles are functionalized with hydrophobic hydrocarbon tails. These hydrophobic groups preferentially bind to microplastics, which can then be extracted using a neodymium magnet by swirling the magnet in the sample jar and then rinsing it into a clean reservoir. Recovery of microplastics from spiked samples is demonstrated on a variety of size ranges from less than 20 µm to greater than 1 mm. It was concluded that magnetic extraction is beneficial as a secondary extraction technique after density separation or for samples that are relatively clean, as in drinking water.[19] Chemical digestion may be used to remove organic material while leaving microplastic particles behind. These methods include wet peroxide oxidation, alkaline digestion, and acidic digestion. When employing chemical digestion, it is important to ensure that the biological tissue and plant matter are removed without affecting the microplastics being collected. Acidic digestion has been shown to break down certain polymers, including nylon, polyamide, and rubber.[20] It has also been demonstrated in a publication by Munno, et al, that high temperatures generated during digestion (> 60° C) can result in the loss of some microplastics, particularly microbeads used in personal care products.[21]

For biological samples, including collection of microplastics from gastrointestinal (GI) tracts, an alternative extraction procedure was developed by the California Department of Public Health, in collaboration with the Rochman Lab, to avoid damage to the microplastics under study and to ensure that no biological tissue remains adhered to the surface of the extracted microplastics. In this procedure, the GI tract is dissected, isolated, and sealed in a vial. The vial is then immersed in a water tank and subjected to bursts of ultrasonic waves, termed pulsed ultrasonic extraction (PUE). The sample is then poured through a 1 mm stainless steel sieve and then filtered using a 10 µm core polycarbonate filter. Compared to samples prepared using traditional KOH digestion, samples extracted using PUE showed much cleaner surfaces and resulted in better spectral matches to reference databases.[22] Biota can be extracted whole, or dissected to isolate the GI tract or target organs.[23]

Once an environmental sample has been collected and extracted, it may be sorted into various size fractions. Sieve stacks are used to separate particles into different size fractions down to approximately 300 µm.[24] For smaller particles, vacuum filtration with progressively smaller pore size membranes may be used. Large microplastics can easily clog filter membranes or obscure smaller particles if size fractioning is not employed. For particles greater than approximately 300 µm, samples may be manipulated manually using fine-tipped forceps, while smaller particles are more difficult to manipulate and can be analyzed directly from the filter membrane.[16] The use of size fractioning provides an additional benefit of collecting particles of similar size, which makes manual sorting easier.

Due to the varied nature of techniques and differing laboratory conditions, it is important to follow standard QA/QC techniques to account for any contamination that may be introduced throughout the collection and extraction process. To limit the amount of contamination, it is best to minimize both the number of people handling samples and the amount of time the sample is exposed to air. General QA/QC lab practices include maintaining clean work surfaces, avoiding synthetic clothing, covering samples whenever possible, and installing air filters in the laboratory.

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In addition, proper QC/QA procedures include the generation of blank samples both in the field at collection and in the laboratory during extraction, which are treated with the exact same procedure used for measured samples. The results of particles found in the blank measurements may then be subtracted from the sample measurements or reported for each study.[8]

Detection and Identification Methods

Visual examination of extracted samples using a stereo zoom microscope is arguably the most prevalent technique for identifying microplastics. Using visual examination, a suspected microplastic can be characterized by color, and morphology. In addition, visual identification can be used to discriminate natural particles from anthropogenic particles. Different modes of imaging can help to improve contrast and aid in identification, including reflected/transmitted light, polarized light microscopy, and dark field microscopy. Microscopy images of the particles can be taken and used to record measurements for exact particle dimensions with the implementation of software such as ImageJ.[25] The reliability of visual examination alone to definitively identify microplastics is low: Depending on the researcher, false negatives and positives may occur with varying frequency.[24] The addition of fluorescent staining can improve identification using optical microscopy. The most common stain used in the identification of microplastics is Nile Red, which binds to plastics in both exposure experiments in the lab and in environmental samples through hydrophobic interactions. Nile Red fluoresces at a variety of wavelengths and is dependent on the hydrophobicity of the microplastic particle's surface. However, certain types of plastics, including polycarbonate, polyurethane, PET, and PVC display weak signals, while microplastic fibers are particularly difficult to stain.[26] In response to these difficulties, alternate stains have been tested in the Rochman Lab, including those designed specifically for textiles. For both laboratory tests and environmental samples, different dyes have been identified as promising stain alternatives (see Figure 2).[27-29]

For definitive chemical identification, there are a number of techniques that may be used, including pyrolysis gas chromatography-mass spectrometry (GC-MS), Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy, and scanning electron microscopy (SEM) plus energy dispersive x-ray spectroscopy (SEM/EDS). The application of these techniques has been described in detail elsewhere,[24] therefore a short overview of each technique's use in microplastics research will be given here. Pyrolysis GC-MS works by thermally breaking down the sample under measurement: The masses of the daughter fragments are analyzed in the resulting pyrogram to

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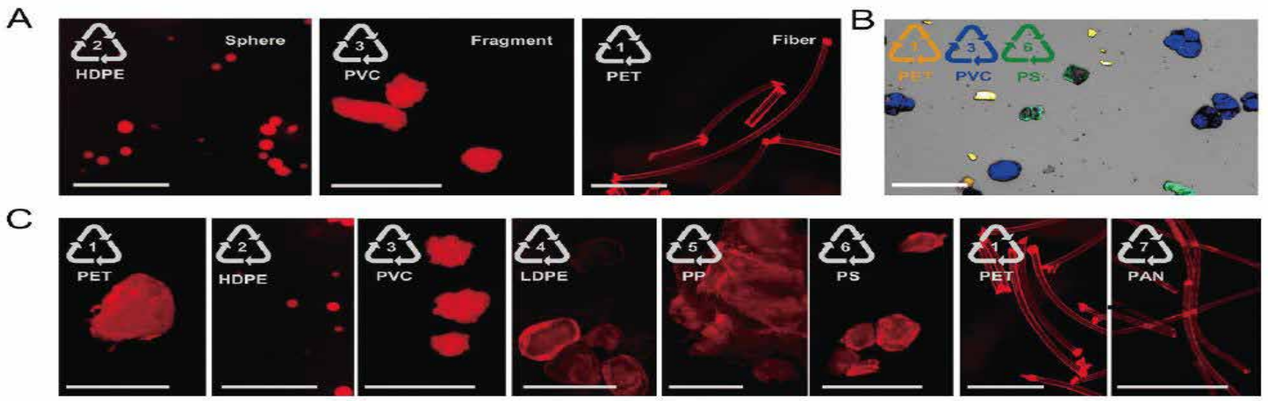

Figure 2: Examples of plastic types and morphologies dyed with different dyes. (A) Different morphologies: Spheres (10-90 µm), fragments (50-300 µm), and fibers (30-60 µm/150-5000 µm) dyed with pink dye. (B) Different fluorophores: Green (Kentucky dye), red (pink dye), and far-red (blue dye). Pseudocolors are applied to different fluorescent channels for the purpose of differentiation. (C) Different polymer types dyed with pink dye: Polyethylene terephthalate (PET) fragments (50-500 µm), high-density polyethylene (HDPE) spheres (10-90 µm), polyvinyl chloride (PVC) fragments (50-300 µm), low-density polyethylene (LDPE) fragments (100-500 µm), polypropylene (PP) fragments (500-4000 µm), polystyrene (PS) fragments (100-300 µm), polyester (PET) fiber (30-60 µm/150-5000 µm), and polyacrylonitrile (PAN) fiber (20-50 µm/300-3000 µm). Scale bars are 550 µm. Reprinted with permission from Environmental Science & Technology Letters (doi: 10.1021/acs.estlett.9b00241) Copyright (2019) American Chemical Society.

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elucidate the parent molecule. GC-MS is considered a "gold standard" in analytical labs, and is a readily available piece of analytical instrumentation. Pyrolysis GC-MS provides simultaneous identification and quantification of microplastics in complex samples. Because of the quantitative nature of this technique (in mass, not number of particles), there is risk of matrix effects from remaining organic matter and materials or chemicals from extraction techniques, so extra care must be taken to accommodate for potential contaminants.[24]

Raman spectroscopy and FT-IR spectroscopy are both techniques that probe the vibrational bonds in a molecule. FT-IR uses broadband infrared light to illuminate a sample; when the light is resonant with a vibrational band in the molecule under study, a decrease in the intensity of the infrared light is observed. In Raman spectroscopy, a monochromatic laser source illuminates the sample; most of the light is elastically scattered (Rayleigh scattering), while a small portion of light is inelastically scattered to lower or higher frequency (Stokes and anti-Stokes scattering). The difference in energy between the inelastically scattered photon and the laser corresponds to a vibrational band in the molecule under study. These two vibrational spectroscopy techniques are complementary and provide different structural information on the particle under study. For example, Raman active vibrational modes can provide information on the backbone of a polymer, while infrared active vibrational modes provide information on side chains. In addition, Raman spectroscopy can provide information on additives and pigments or dyes in microplastics, which can help in tracking the source of microplastics. While micro-FT-IR spectroscopy can measure a minimum particle size of approximately 10 µm, Raman spectroscopy can measure particles down to < 1 µm in size.[24] For microplastics, this is critically important because it is generally agreed that, as particle sizes become smaller, the abundance of microplastics increases. Smaller particle sizes also have bigger ramifications when it comes to toxicology, which will be discussed in more detail below.[24,30,31]

SEM/EDS combines scanning electron microscopy and energy dispersive x-ray spectroscopy to provide high resolution imaging at the nanoscale with elemental characterization of heavier elements. SEM focuses an electron beam onto the sample under study and measures the resulting scattered electrons. EDS works in combination with SEM and measures the resulting x-ray radiation from the sample. SEM/EDS provides a means to quickly distinguish plastics from minerals, which in marine environments, are primarily Si (sand) and Ca (shell fragments).[22,24] Each technique described above has advantages, disadvantages, and varying associated costs and measurement times. In the characterization of microplastics, it is important to note that multiple techniques may be required for complete characterization.[24] It is also important to standardize methods across different laboratories to ensure consistency in reporting. This is one of the main goals of the microplastics study plan organized by the Southern California Coastal Water Research Project (SCCWRP) described in a separate article.

As a single microplastics sample can contain hundreds or thousands of particles, a critical part of the process of standardization is automation of sample measurements, in order to reduce the time required for sample analysis. One such method of automation relies on the use of the optical image of a sample, for example, microplastic particulate on a filter membrane, to distinguish particles from the background substrate. The optical image provides the spatial contrast needed to identify the particulate, and then the use of a motorized stage, together with Raman or FT-IR spectroscopy, allows the user to collect spectra at each isolated particle. Using this technique, large areas can be covered without collecting spectra from areas that are not of interest, for example from the filter membrane itself.[32]

While automated routines like those described above are sufficient for analysis of larger microplastics across an entire filter membrane (for example a 47 mm diameter filter), for analysis of particulate in the lower size range, <20 µm, measurements across an entire filter becomes prohibitively expensive in both time and data size. As part of standardizing the analysis of microplastics, it is important to formulate sampling and sub-sampling schemes that are representative of the sample under study. There are a number of different ways to define sub-sampling, for example, by percentage of filter area covered in a measurement, or by the percentage of total particles measured. In a paper published by Anger, et al, it was proposed that sub-sampling by percentage of total particles is most appropriate for two reasons; one, particles may not be evenly distributed across the filter and two, different filter diameters may be used across different laboratories. The proposed working method was to first estimate the total number of particles on a filter using the optical image, and then chemically identify a chosen subset of particles.[33]

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Once spectroscopic measurements are complete, it is necessary to determine the number of unique components present. Understanding the complete picture of chemical signatures can provide an indication of the source of microplastics and potentially provide information on possible contamination, as well (see Toxicology section).[8] Multivariate analysis techniques including principal component analysis (PCA), multivariate curve resolution (MCR), and cluster analysis techniques can be used to determine the number of unique spectral signatures in a sample set.[34] Once a model has been built, spectral matching algorithms may be used to identify the exact species present in a microplastics sample. The development of spectral databases specific to microplastics can improve the quality of spectral matching and produce results that are more relevant to environmental samples, as microplastics encompass a diverse suite of polymers, additives, and dyes/pigments . Existing libraries contain mostly pure polymers, which can only provide limited information. The development of SLoPP and SLoPP-E (Spectral Library of Plastic Particles, Environment) libraries by the Rochman Lab enable better spectral matching and provide much more information on collected samples, as the libraries include reference spectra from particles sourced from everyday products and from the environment.[35] Making these databases freely accessible to the microplastics community helps to ease the cost burden of commercial spectral databases, which frequently come with high annual subscription costs.

Toxicology

While it is important to understand the presence and nature of microplastics in our environment, it is also critically important to understand the impact of microplastics on our ecosystems and potentially on human health, as well.

There are a number of mechanisms through which microplastics may be harmful, including physical and chemical pathways, as described above. Because microplastics can both sorb contaminants[36] and leach harmful additives,[37] bioaccumulation of these toxins may occur in marine organisms.[38] In addition, biomagnification, where toxins consumed by smaller organisms are concentrated in predators that consume them, can also occur, affecting the health of ecosystems across the entire food web.

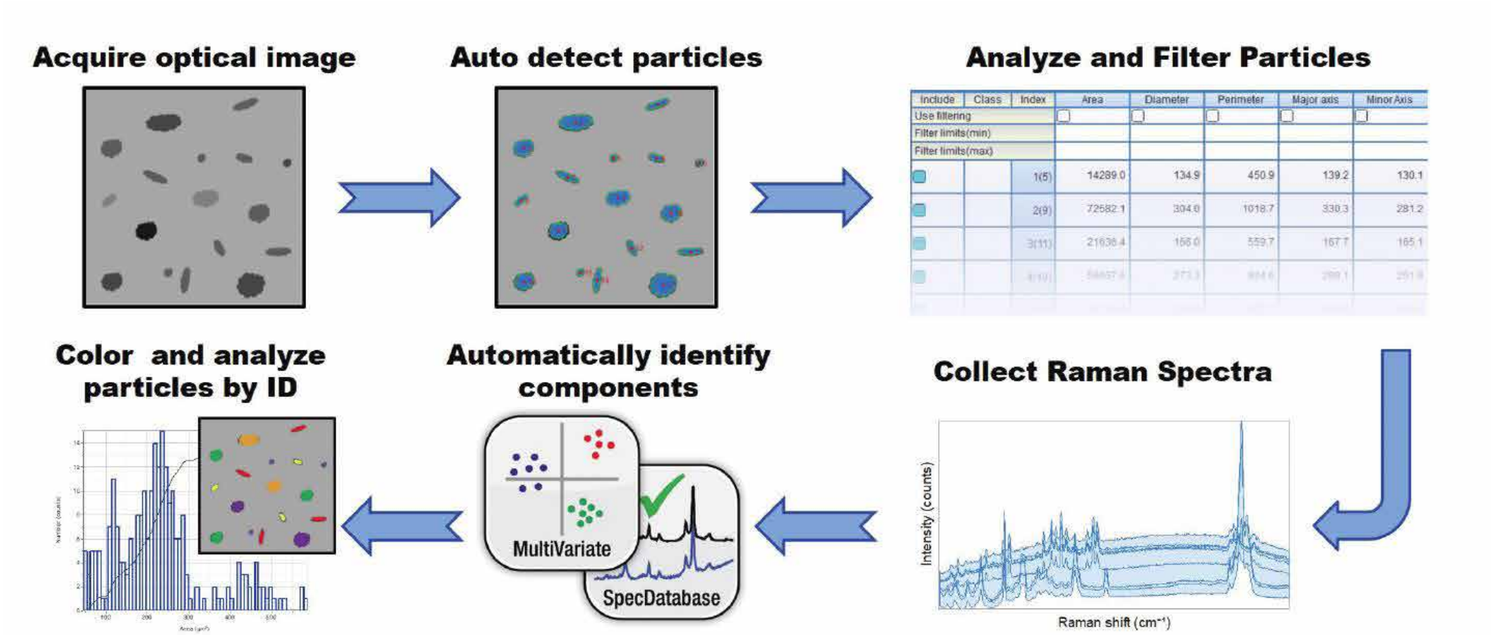

Figure 3: Example workflow for automation of microplastic measurements using Raman spectroscopy and HORIBA's ParticleFinder software module.

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Examples of chemical contaminants in microplastics (sorbed contaminants, chemical ingredients, and chemical byproducts) are shown in Figure 4.[39]

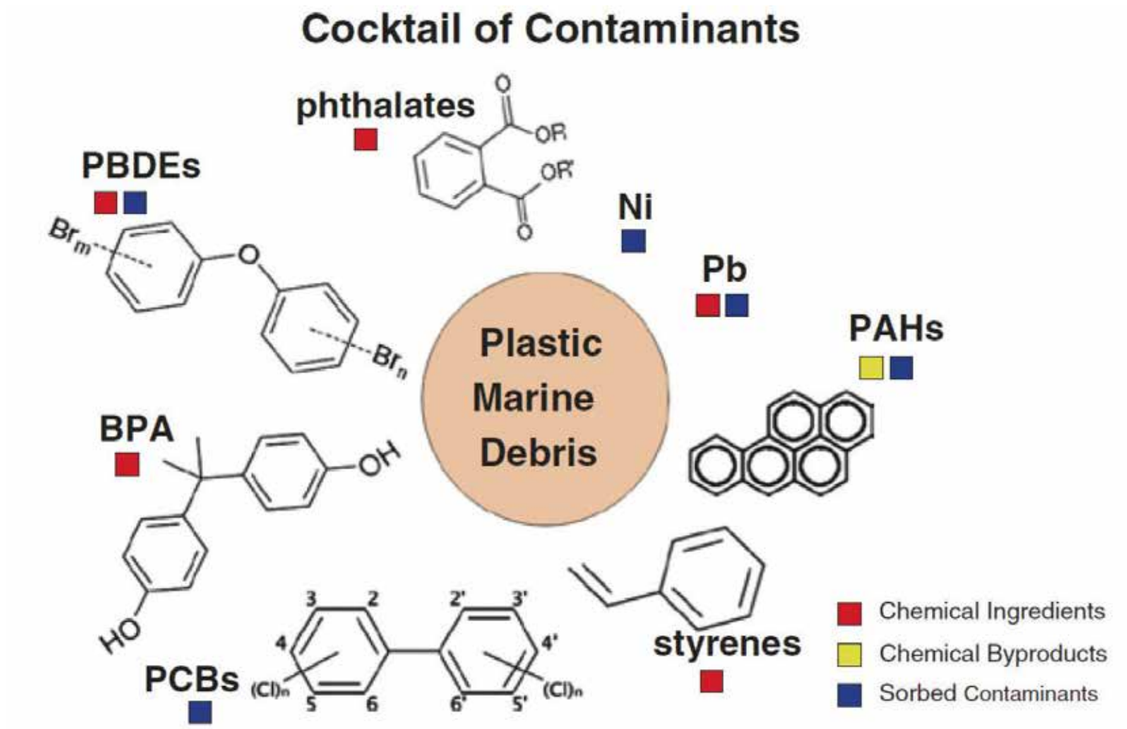

Figure 4: Cocktail of contaminants associated with marine plastic debris. Contaminants associated with marine debris include chemical ingredients (red squares), byproducts of manufacturing (yellow squares) and those that accumulate from surrounding ocean water in the marine environment (blue squares). Reprinted with permission from Marine Anthropogenic Litter (doi: 10.1007/978-3-319-16510-3).

In a laboratory-based study by Rochman et al, the effects of bioaccumulation were tested using Japanese medaka.In this study, three groups of fish were studied; a control group, a group fed virgin LDPE, and a group fed LDPE that had been deployed in an urban bay. After one and two months of exposure, the amount of polycyclic aromatic hydrocabons (PAH), polychlorinated biphenyls (PCB), and polybrominated diphenyls (PBDE) were tracked in the tissue of the fish. The results showed that not only does bioaccumulation of chemical pollutants occur, but signs of liver toxicity and pathology arise in the groups fed both virgin and deployed LDPE, namely glycogen depletion, fatty vacuolation, and single cell necrosis (in deployed LDPE only). This study demonstrated that (1) bioaccumulation of chemical pollutants through exposure to microplastics occurs in aquatic organisms, and (2) exposure to microplastics and associated chemicals may induce hepatic stress.[40]

While evidence for harm from microplastics in marine life has been well documented,[12,39-44] less well understood is the effect that microplastics may have on humans. It is clear that microplastics are found in food consumed, including a variety of species of marine organisms,[45] salt,[46] and canned fish.[47]
An example of a potential route of exposure through seafood is shown in Figure 5.[14]

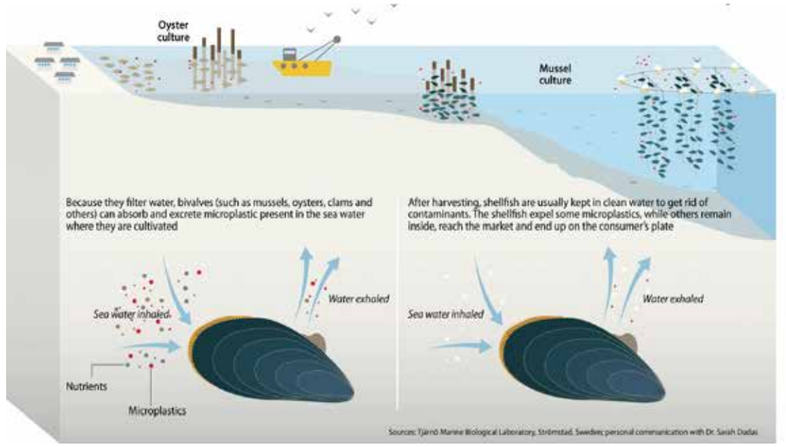

Figure 5: An example of how microplastics could end up on a consumer's plate.
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What happens once microplastics are consumed is not entirely clear. It is likely that many microplastic fragments are passed as waste, but this does not negate the possibility of physical and chemical toxicity in humans. A well known example of the effect of chemical toxicity from plastic packaging is bisphenol-A (BPA), a constituent monomer of polycarbonate. It was demonstrated that higher levels of BPA present in urine samples were associated with reported heart disease in American adults.[48] Further research is needed to understand the amount of microplastics consumed, associated chemical exposure, and what health effects arise from such exposure.[14]

Mitigation

To address the global problem of microplastics, governments around the world have begun to enact policies to deal with the staggering problem of plastic pollution. This includes the ban of microbeads from personal care products, the tracking of municipal or commercial waste, and commitments to reduce marine debris.[14] From an industrial perspective, companies have started to implement sustainability practices, including manufacturing products from plastics collected from beaches[49], moving towards biodegradable or compostable materials,[50] and transitioning to durable, multi-use packaging.[51] Beach clean-up programs organized by non-governmental organizations (NGO) serve two purposes: To raise awareness of the,problem of plastic marine debris and to help remove larger plastics that have the potential to become smaller plastics emissions, where hundreds to thousands of microplastics are generated through the washing of a single garment. [53] Products like the Lint LUV-R filter and CORA ball can help to trap microplastic fibers before they reach wastewater treatment plants, and ultimately are discharged into bodies of water.[9]

Conclusion

Microplastic pollution is a global issue, and one of the first steps in addressing the problem is to understand the nature of microplastics. This includes elucidating the major sources and sinks of microplastics in the environment, types of plastics and additives, and the particle morphologies and sizes. Optimization and standardization of laboratory methods for microplastic analysis is critical for reproducibility amongst labs, including sample collection, extraction, detection, and identification methods. From this information, researchers can understand more about the sources of microplastics and how best to mitigate the threat to the environment, and potentially to human health as well. The work of research laboratories like that of the Rochman group are critical to help drive standardized methodologies and a true understanding of the impact of microplastics and nanoplastics on our environment and health. Only through the development of harmonized reproducible methodologies will government agencies be able to provide the necessary recommendations to state and federal legislative bodies to put in place mandated monitoring and control programs.

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* This content is based on our investigation at the year of issue unless otherwise stated.

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Understanding the nature of microplastic pollution and identifying environmental impacts, cont.

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Bridget O'DONNELL, Ph.D.
Manager of Raman Applications HORIBA Instruments Incorporated (HII)

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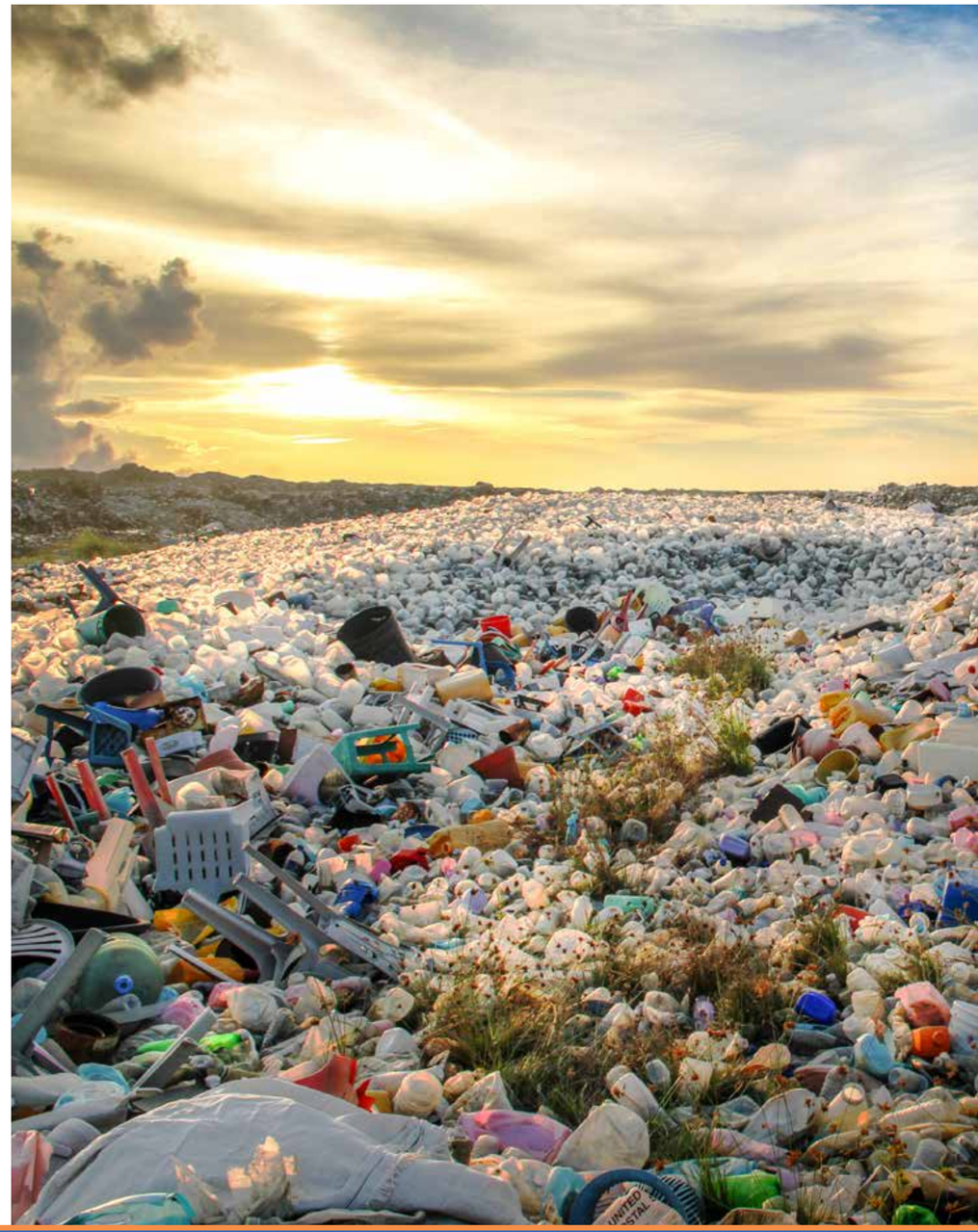
HORIBA is working with several key opinion leaders to help develop and drive critical thinking to establish analytical standards and regulation guidelines.

Raman applications on microplastics

Microplastics (MPs) is an emerging and rapidly growing research field, the potential for which the scientific impact and business opportunities are abundant. HORIBA is working with several key opinion leaders (KOLs) to help develop and drive the critical thinking to establish analytical standards and regulation guidelines. The availability of harmonized methods and key instrumental and software capabilities will determine how well we can monitor and control MP pollution and health risks in the future. This paper will summarize ongoing collaboration projects with KOLs being performed by the HORIBA US Raman team, and what we've learned so far.

It has been reported that less than 10% of manufactured plastics are recycled. With approx. 30% in use, this leaves 60% of plastics to be discarded into environment, or being incinerated. Discarded plastics take tens (e.g. plastic bags and foam cups) to hundreds (e.g. plastic bottles and disposable diapers) of years to decompose, accumulating on land, including in landfill sites, coastlines, in Arctic sea ice, and on the sea surface and floor.[1] During these long years, plastics fragment into small particulates, forming microplastics (MPs) and nanoplastics (NPs). They are not only hazardous for wildlife, but also pose health risks for humans[2] through air pollution (e.g. nanotoxicity due to inhaling NPs), water (e.g. MPs in drinking water) and food sources.

Governing bodies around the world have recognized the detrimental impact of MPs, and started implementing new regulations. Scientific guidelines are critical for effective regulation, and key opinion leaders (KOLs) are actively working to develop standard methods for sample collection, preparation, analysis, and evaluation. HORIBA has been working with several KOLs to understand analytical requirements for MPs, including software and hardware optimization and automation. These efforts have been successful so far, resulting in various publications and presentations[3]. There is, however, still a long way to go.



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Raman applications on microplastics, cont.

It has been demonstrated[4] that using multiple technologies, including Raman microscopy, is essential to identifying MPs without ambiguity. Raman microscopy is growing in its importance due to its high spatial resolution (necessary for particles on the order of ~ 10 µm and smaller), high tolerance toward wet samples (advantageous for field analysis), sensitivity to additives (useful for brand and source identification) and polymers (useful for chemical identification), and specificity for polymer type (for positive identification) and minerals (for exclusive identification). HORIBA Scientific's XploRA PLUS confocal Raman microscope is well equipped to handle MP analysis, and has been installed at multiple KOL laboratories, successfully proving its performance and usefulness. As research progresses, the demand for Raman analysis (and instruments) will expand to field analysis instruments (e.g. compact Raman spectrometers, such as HORIBA's MacroRAM coupled with optical fiber probes), NPs analysis (e.g. AFM-Raman hybrid system) aided by nano-tags (e.g. nanoGPS), and multi-modal imaging and microscopy (e.g. epi-fluorescence and hyperspectral imaging microscopy). HORIBA is well placed to explore the business potential of MPs with its versatile collection of products.

Importance of collaboration

MP analysis is just emerging and rapidly growing as a research field; exponentially increasing in volume and importance as an application area with critical timing as a business opportunity. Analytical requirements are not well determined, yet. Standards and regulations are yet to be defined. It is critical to work with KOLs to accumulate and exchange knowledge, learn requirements specific for MP analysis, establish Raman as a standard analysis technology for MPs, and establish and brand HORIBA as the go-to vendor for Raman analysis for MPs.

Collaboration with Prof. Chelsea Rochman, University of Toronto[5]

Professor Rochman is a faculty member in the Department of Ecology & Evolutionary Biology at the University of Toronto. The ultimate goal of this collaboration is to develop an automated technique for handling small-size MPs (< 100 µm).

Automating MP analysis must be proceeded by establishing standard operating procedures (SOPs). SOPs are critical in MP analysis because MPs migrate over a long distance (e.g. from river to ocean to shore), and require collective characterization by multiple research groups.

(a) (b) (c)

Figure 1: HORIBA Raman instruments. (a) XploRA PLUS, (b) MacroRAM and (c) XploRA Nano

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Raman applications on microplastics, cont.

Unless every research group follows the same SOP, it will be impossible to combine/compare data, follow the plastics lifecycle as they migrate through the environment, or establish effective guidelines to minimize MPs in the environment. Dr. Rochman's group has developed SOPs for sample preparation that include:

MPs are collected from various matrices (water, sediment, biota)
1. Acid, base, or enzymatic digestion is carried out to remove organic material
2. MPs are size fractioned using sieves down to 100 µm in size
3. Remaining small MPs are filtered into size groups down to 1 µm

When collected from the environment, MP samples contain inorganic materials (e.g. sand), organic materials (e.g. biofilm), and non-synthetic materials (e.g. natural fibers) along with MPs. SOPs developed by Dr. Rochman's group separate MPs from non-plastic materials (step 1 of SOP), and divide MPs into size groups (steps 2 and 3 of SOP). Step 2 divides MPs into multiple size categories using sieves, the smallest size category being 100 µm in diameter. Particles smaller than 100 µm are divided into multiple size categories using filters in step 3, the smallest size threshold being 1 µm in diameter. It is not an accident that size thresholds are set at 100 µm and 1 µm. 100 µm represents the smallest size a researcher with a reasonable training can handle manually (e.g. picking up with tweezers). In other words, step 2, with the smallest sieve, separates MPs that can be manually sorted from those too small for that, and designates them for further sample preparation in step 3.
1 µm represents the smallest size an optical microscope can detect, resolve, count, and measure. In other words, step 3, with the finest filter, separates MPs that can be analyzed with an optical microscope i.e. 1 µm or greater, from those too small for that, i.e. < 1 µm, and designates those < 1 µm for nanomaterial analysis by, for example, an atomic force microscope (AFM).

Dr. Rochman's group recognized the advantage of minimizing the number of sample transfers, and utilized filters as a substrate to present the sample to Raman microscopes. This opened the door to further research to optimize the filter material for step 3. Currently multiple filters, commercial and custom developed in the lab, are tested for their efficiency in terms of interference, cost, mass manufacturing, etc.

As the Rochman group's SOPs are being finessed for practicality, the volume of samples they analyze increases, and so do their data accumulation flowchart of MP analysis, as seen in Figure 2. Items highlighted in red mark pro- challenges. They have started compiling accumulated data into Raman spectral libraries dedicated for MPs research called SLoPP (spectral library of plastic particles) and SLoPP-E (spectral library of plastic particles aged in environment)[6]. SLoPP is made of pure and pristine MPs spectra, and SLoPP-E spectra of weathered MPs. These libraries are being continuously expanded.

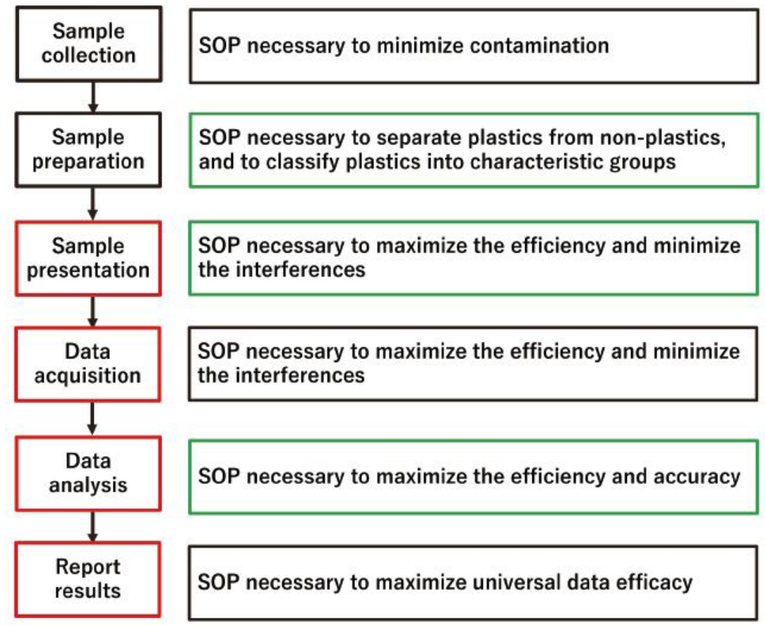

Figure 2: A flowchart of MP analysis. Items highlighted in red mark processes of high demand for automation. Items in green mark Rochman group research focuses at this time.

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Raman applications on microplastics, cont.

Collaboration with Dr. Ashok Deshpande, NOAA, and Dr. Jennifer Lynch, NIST

Raman is a relatively new technology for MP analysis, gaining recognition in recent years. It is important to evaluate a new technology with respect to existing technologies. For MP analysis, the two methods used are mainly pyrolysis gas chromatography-mass spectrometer (pyro-GC-MS) and Fourier transform infrared (FT-IR) spectroscopy. MP samples from Hawaii were analyzed by three technologies for comparison, each at a different laboratory using a different technology. The results proved not the superiority of a single technology, but the importance of multi-technology analysis for accurate identification. Dr. Jennifer Lynch of the Biochemical and Exposure Science Group of the National Institute of Standards and Technology (NIST)[8] is a Research Biologist at, and co-director of the Center for Marine Debris Research (Hawaii Pacific University). She provided samples in this collaboration, and her student Kayla Brignac performed the analysis using FT-IR. Dr. Ashok Deshpande of the National Oceanic and Atmospheric Administration (NOAA)[9] is a Research Chemist at the Northeast Fisheries Science Center (James J. Howard Marine Sciences Laboratory at Sandy Hook). He performed the analysis with pyro-GC-MS. Dr. Bridget O'Donnell of HORIBA is Manager of Raman Applications at HORIBA Scientific (Piscataway, New Jersey). She coordinated the collaboration, and performed analysis using Raman.

• Identification was 'perfect' for approximately 70% of samples, all three technologies making the same identification, and boosting the confidence in the results by cross-validating each other.

• Identification was 'good' for approximately 10% of samples, two technologies making the same identification. The third technology identifies these as a variety of, or similar structure to, the accurate identification.

• Identification was 'poor' for approximately 10% of samples, each technology making different identification.

• The remaining 10% of samples were identified by only one technology, the other two technologies failing to yield usable data.

Figure 3: Photo of Hawaiian marine debris items, Windward Oahu beach. Kahuku Transect 1[7]

	Raman	ATR-FT-IR	Pyro-GC-MS
Technology	Scattering technique	Absorption technique	Chromatographic technique
Sample	Little to no sample preparation	Sample mounted on diamond crystal and compressed	Sample is completely pyrolyzed (destroyed)
Advantages	Sensitive to molecular vibration based on change in polarizability Sensitive to polymer backbone structure Spatial resolution < 1 µm	Sensitive to molecular vibration based on change in dipole moment Sensitive to polymer side chains Extensive databases available	Sensitive to molecular structure based on breakdown into fragments Quantitative results
Disadvantages	Susceptible to background fluorescence	Susceptible to water absorption	Long measurement time Large sample volume
Analysis by	Bridget O'Donnell, HORIBA	Jennifer Lynch, NIST	Ashok Deshpande, NOAA

Table 1: Comparison of pyro-GC-MS, FT-IR and Raman

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Raman applications on microplastics, cont.

Given the extreme heterogeneity of plastic products with diversity in manufacturing process, this is not surprising. It would be possible to improve these results with further analysis or additional analytical technologies, and calls for adding even more technologies for the MPs' analytical tool box.

Collaboration with Southern California Coastal Water Research Project (SCCWRP)

Southern California Coastal Water Research Project (SCCWRP) [10] is a public Research and Development agency that is leading the project to establish the guidelines for MP analysis, which will become the standard method for California State Government regulations. Dr. Steve Weisberg (Executive Director) and Dr. Charles Wong (Department Head, Chemistry Department) initiated and organized a study plan to evaluate MP measurement methods. This is the first step in establishing standard measurement methods that every MP research group will share and follow. In this study plan, they invited researchers around the world, including HORIBA, to participate in drafting measurement methods. SCCWRP has completed drafting a proposal for the method, and is in the process of producing and distributing standard samples in clean water, dirty water, sediment, and biological tissue. Each of the participating laboratories will analyze standard samples with the proposed method, evaluate its practicality, and help finesse improvements.

HORIBA contributes expertise on Raman spectroscopy by proposing an augmentation to the study plan, and will evaluate methods for automating MP analysis and for potential field analysis using optical probes.

In preparation for and as a part of the study plan, SCCWRP organized three events in 2019: A workshop and round table discussion in April, sample extraction and preparation training in October, and sample analysis training in November. HORIBA participated in all three events, playing a key role in the sample analysis training.

Many environmental researchers spend limited time in a chemical laboratory, and thus require training operating analytical instruments. The training session at SCCWRP for sample analysis in November 2019 was dedicated to Raman microscopy (provided by HORIBA Scientific) and FT-IR microscopy (provided by Thermo-Fisher). Researchers from key regulatory (e.g. Environmental Protection Agency) and academic (e.g. California State Universities) institutions were present, and trained on Raman using HORIBA Scientific's XploRA PLUS. Researchers will travel back to SCCWRP to perform Raman analysis as part of the study plan, when standard samples are distributed, using the XploRA PLUS.

Instrument requirements of Raman analysis for MP analysis

One of the biggest complexities of MPs (and NPs) analysis is the extremely wide size distribution, ranging from 5 mm to 1 µm (and smaller). As mentioned above, one of the first steps of sample preparation SOPs are classifying MPs into size groups.

MacroRAM with BallProbe[11] (by MarqMetrix) would be suitable to analyze large MPs (in the order of millimeters), especially for field screening. Handheld Raman may be an intuitive candidate for field screening, but is typically designed for bulk analysis. Its measurement spot may be too large for MPs. The focus point of BallProbe is small (in the order of 200-400 µm), making it a good match for large MPs in size. The MacroRAM is small, light and rugged, and suitable to transport between field basecamps. There are no moving parts, so installation is minimal and alignment is not required; plug it in, and turn it on.

One of the important aspects when selecting a field unit is its compatibility to a lab unit. MPs are sent back to a lab for further analysis if their analysis results are unsatisfactory for various reasons (e.g. too small even for the BallProbe, inconclusive identification, possibility of toxicity, etc.). It simplifies data comparison when the field unit and the lab unit use the same software. HORIBA's benchtop MacroRAM, just like all Raman instruments from HORIBA, uses the LabSpec 6 Spectroscopy Suite (LS6) software, making it easy and simple to compare data to those from a lab unit such as the XploRA PLUS.

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Raman applications on microplastics, cont.

XploRA PLUS confocal Raman microscope is well equipped to handle small MP analysis (typically smaller than 1 mm down to less than 1 µm) with a fully featured optical microscope, multiple lasers, confocal spectrometer, motorized stage, and advanced software. The first step of any analysis is to observe MPs to gauge their color, size, shape and texture. For small MPs (typically smaller than 1 mm), the observation requires an optical microscope. Optical microscopy technologies are dedicated to improving the contrast and the image authenticity. It may sound simple, but it is not trivial to improve contrast or image authenticity. To improve the contrast, one must improve the signal-to-noise ratio (SNR), achieve the best possible focus, and be able to differentiate subtle differences in optical properties (e.g. color, refractive index, birefringence, etc.). To improve image authenticity, one must minimize interference, such as 'shadows' from non-uniform illumination, artifacts and distortions from optics themselves, and aberrations from polychromatic light. HORIBA's XploRA PLUS is compatible with all optical microscopy technologies, such as darkfi eld (DF) imaging, polarized light microscopy (PLM), epi-fl uorescence imaging, and hyperspectral imaging (HSI) microscopy, allowing the researcher to observe, analyze and classify MPs by their size, color, shape and texture. It is imperative to note that there is absolutely no sample transfer to utilize any or all of these multimodal imaging techniques, which improves the practicality, speed and reliability of correlated analysis immensely.

Chemical composition of synthetic plastics are complex with multiple polymers and additives[12] such as stabilizers, flame retardants, pigments, reinforcements, etc. The complexity increases as MPs undergo weathering in environments, which changes the physical and chemical characteristics. It has been reported[13] that the impact of weathering on MPs is signifi cant, and that the accuracy improves a great deal when spectra from weathered MPs, as well as those from pristine plastics, are used in identification methods. Optimum experiment conditions, naturally, vary depending on MPs' characteristics, the first of which is selecting the 'right' laser to suppress any fl uorescence baseline. The XploRA PLUS can house three lasers from blue to near-infrared (NIR), and switch between them easily with a single click, making laser selection a quick and intuitive operation.

One of the most neglected steps in MP analysis is sample presentation. It is necessary to place MPs on some kind of substrate to present it to a Raman microscope. The substrate may be a petri dish, a glass slide or a filter on a filter holder. It is possible to get interference from substrates. For example, the substrate may be Raman active, and its spectral features mix with MP spectra. Confocality of the spectrometer suppresses signals from substrates by suppressing out of focus signal. The XploRA PLUS employs a true confocal optical design for the Raman scattering beam path, making it ideal to acquire 'clean' Raman spectra by minimizing non-sample signals.

As Dr. Andrew Whitley's article in this issue of Readout mentioned, assessing MPs in environments for their quantity, migration and hazard requires statistical analysis of a massive amount of MPs. Automated high throughput analysis is absolutely necessary, and a critical research goal. While research groups, with collaboration with HORIBA, are developing SOPs to become the template of automated analysis, a few elements are already identifi ed as necessary. MPs are often presented for analysis arrayed in a petri dish or retained on a filter. The size of a petri dish or a filter is much bigger than MPs, and navigation requires that the stage travel a long distance while stopping at precise positions. A motorized stage with precision control makes navigation easier and more precise, making the experiment more efficient.

Another advantage of a motorized stage is software control and programmed movements. Coupling this ability to the microscopy functionalities of the XploRA PLUS, HORIBA developed an application module called ParticleFinder (PF)[14] on the LS6 platform. PF acquires a microgram, and analyzes the counts, sizes, shapes, and locations of MPs. PF then moves the stage to each of the MP's location, and acquires a Raman spectrum. The final results include total counts of all MPs, statistics of sizes and shapes, locations and Raman spectrum of each MP, and spectral classifications.

As mentioned repeatedly, MPs are highly complex and heterogeneity targets for analysis. Data processing and analysis are proportionally complex[15] requiring sophisticated software. LS6 offers extensive functionalities for data processing (e.g. baseline correction, smoothing, substrate spectrum subtraction, etc.), data analysis (e.g. multivariate analysis, library search, etc.) and visualization (e.g. image rendering) both developed in house and working with business collaborators: Wiley Science Solutions, to incorporate KnowItAll® library search, and Eigenvector Research Inc. for multivariate analysis (MVA).

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Raman applications on microplastics, cont.

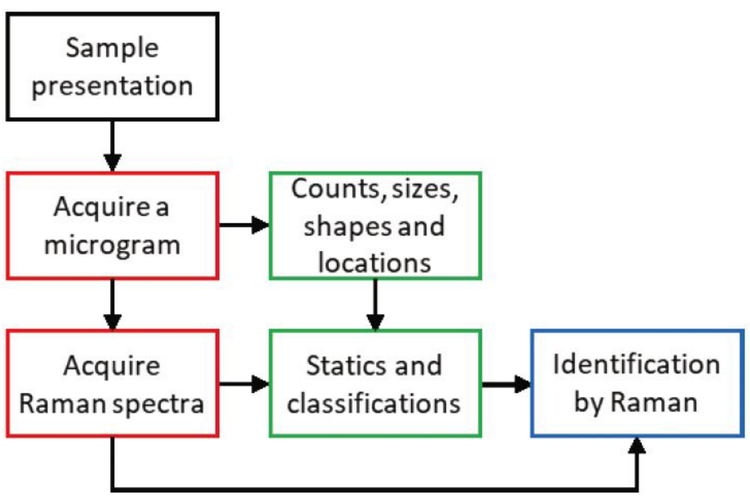

Figure 4: Workflow diagram of PF operation followed by identification by Raman library search. Red boxes highlight data acquisition steps in PF, green boxes hightlight results generated in PF, and blue boxes highlight results coupled with library search.

HORIBA technologies for MPs analysis

The complexity and heterogeneity of MP analysis requires, as demonstrated in the collaboration work with NOAA and NIST above, multimodal imaging and multitechnology approaches. It has, therefore, become a natural focus of interest how to combine, correlate and compare data and results from multiple sources. For now, we are still tackling data from one technology at a time. However, we are preparing for next steps, investigating future development possibilities such as data fusion, correlated microscopy and machine learning.

Conclusion

Microplastics (MP) is a mega trend that is growing even bigger. HORIBA is collaborating with KOLs in the field to determine (and influence) the market demand (and trend), and staying relevant to this newly emerging field. We have made an impression as 'the' Raman company for researchers who will provide guidelines to MPs, regulations. The scientific and business opportunities are abundant, and we are making good progress.

* This content is based on our investigation at the year of issue unless otherwise stated.

Raman spectroscopy	Fluorescence spectroscopy	Particle size analysis	EDXRF† spectroscopy
Chemical identification & differentiation of: • Polymers • Additives • Dyes/Pigments • Natural particles	• Probe effect of MPs on DOM* • Determine concentration of NPs • Quantify MPs for toxicity studies • Measure DOM in control studies	• Measure particle size distribution of possible MPs • ViewSizer - Potential for nanoparticle tracking analysis for NPs	• Analyze metals accumulated on MPs[16]

* DOM stands for dissolved organic matter
† EDXRF stands for energy dispersive x-ray fluorescence

Table 2: Summary of HORIBA technologies useful for MPs analysis

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Raman applications on microplastics, cont.

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Recycling of abandoned fishing gear is enabled by spectral identification of polymer types using HORIBA's MacroRAM.

Raman polymer identification of fishing gear using Raman spectroscopy

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Plastic pollution from fishing gear is a global problem that harms the environment. Recycling of damaged or abandoned fishing gear is one way of mitigating the issue, however the exact nature of the polymer must be known in order to identify the correct recycling stream. In this paper, the MacroRAM benchtop Raman spectrometer with remote BallProbe® is used to quickly identify plastics used in various gillnet samples. Raman spectroscopy is demonstrated to be an excellent technique for identifying not only different types of polymers, but also different variants within a polymer class and additives including pigments.

Keywords

Microplastics, pollution, environment, polymer, Raman, remote sampling

Introduction

Plastic pollution is a global problem with harmful effects on ecosystems at all levels of the food web. The disposal of fishing gear specifically is a large contributor making up approximately 85% of plastic pollution found in marine environments.[1] In addition, nylon fishing line and nets are some of the longest-lived plastics with lifetimes ranging in the hundreds of years.[2] To help mitigate the problem of plastic pollution from fishing gear, organizations like *Net Your Problem* collect damaged or abandoned nets, organize and sort them, and ship them to facilities where they may be recycled into pellets for commercial use.[3]
A critical part of this process is accurately identifying the type of polymer the fishing net is composed of so that it may be sorted into the correct recycling stream (e.g. nylon, polypropylene, polyethylene). Nylon, in particular, can be challenging to identify definitively as there are multiple varieties of nylon that may be used in fishing gear. Unambiguously determining the exact type of nylon is an important step in the sorting process.

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Raman polymer identification of fishing gear using Raman spectroscopy, cont.

Raman spectroscopy has been demonstrated as an excellent technique for distinguishing between various types of polymers and within polymer classes, such as nylon. Raman spectra of nylon are unique enough that a high resolution Raman microscope is not required for definitive identification. Figure 1 shows spectra of reference nylon materials recorded with HORIBA's MacroRAM benchtop Raman spectrometer. Each of the polymers display clearly distinguishable spectral fingerprints that allow for identification of unknown samples, including abandoned fishing gear.

Experimental Methods

In this study, a set of four monofilament gillnets and one polytwine gillnet were submitted for analysis using Raman spectroscopy (see Figure 2). The samples were collected by the Cape Cod Commercial Fisherman's Alliance and originated from various states in southern New England (Massachusetts, New Hampshire, and Rhode Island).

HORIBA's MacroRAM benchtop Raman spectrometer was coupled to a BallProbe® (1/8", MarqMetrix®) to enable rapid, alignment free Raman characterization and identification of the unknown polymer types. Near-infrared 785 nm laser excitation was employed to suppress fluorescence induced by the pigmented fibers (white, red, green, and blue).

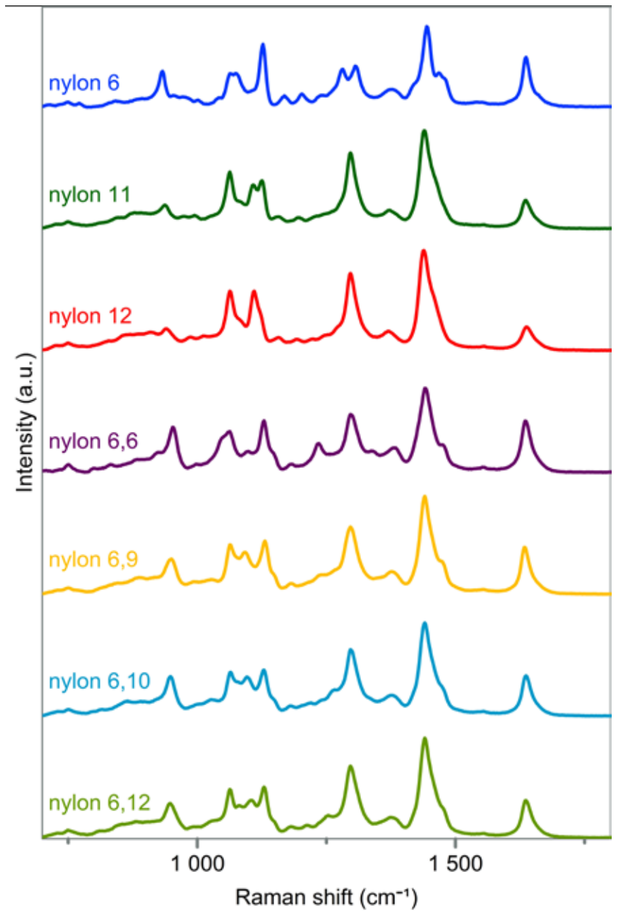

Figure 1: Raman spectra of nylon 6, nylon 11, nylon 12, nylon 6,6, nylon 6,9, nylon 6,10 and nylon 6,12 recorded with HORIBA's MacroRAM benchtop Raman spectrometer. Reference nylon materials were sourced from PolySciences, Inc.

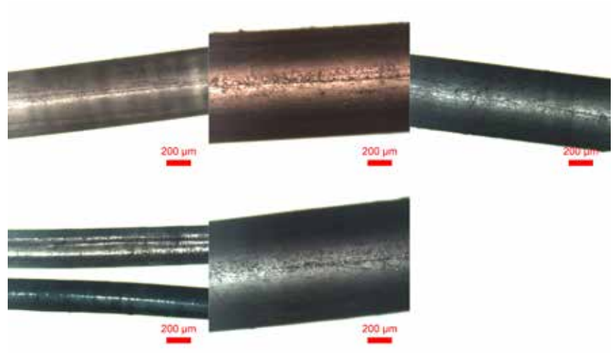

Figure 2: Optical micrographs recorded of various fiber samples; white monofilament gillnet, red monofilament gillnet, green monofilament gillnet, green polytwine gillnet, and blue monofilament gillnet (from top left to bottom right).

Results and Discussion

Spectra recorded from the monofilament samples indicate that all of the samples are comprised of the same variety of nylon. Upon close comparison of the unknown spectra and the nylon reference material spectra, it becomes clear that all of the monofilament samples are assignable as nylon 6. Figure 3 shows the processed spectra of each of the unknown samples after baseline subtraction in addition to the reference spectra of nylon 6 (top) and nylon 6,6 (bottom). In particular, the doublet at ~ 1300 cm-1 is a clear indicator of the assignment to nylon 6 over any other variety of nylon.

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Raman polymer identification of fishing gear using Raman spectroscopy, cont.

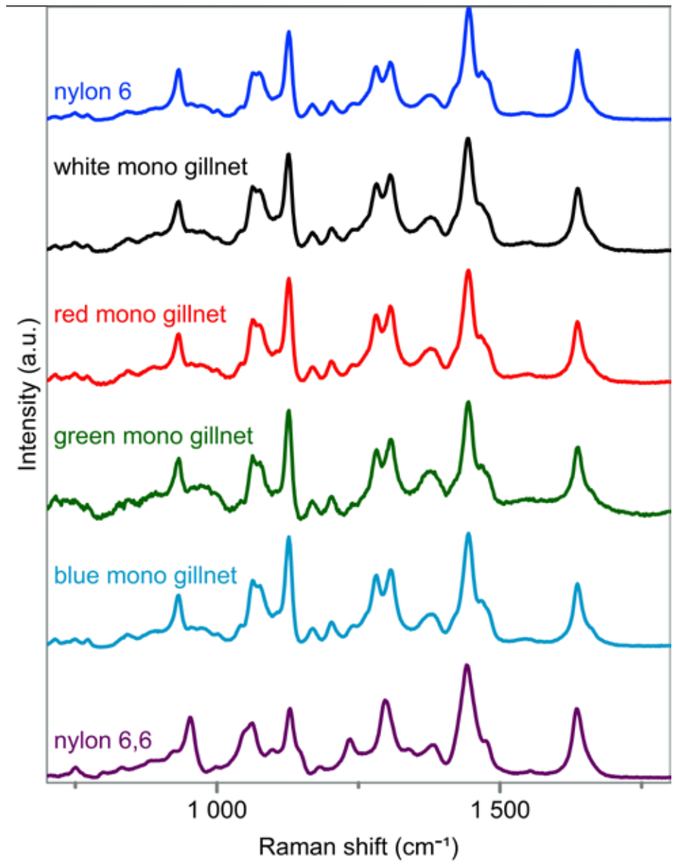

Figure 3: Reference spectra of nylon 6 and nylon 6,6 are shown at the top and bottom, respectively. The spectra of unknown monofilament gillnet samples are plotted in the middle labeled by color (white, red, green, blue).

The green polytwine gillnet sample proved to be more complex. Polytwine gillnets are comprised of multiple filaments interlaced together to form a braid. Upon unravelling the braid, it was clear that there were two different types of filaments making up the polytwine; a lighter colored, slightly thicker set of filaments at the center, and a set of darker color, thinner filaments around the edge. A small sample of each type of filament was trimmed from the polytwine for analysis. Upon measure-ment of the Raman spectra, it became clear that the same spectral bands were observed in both filaments. However, there was a clear difference in the relative intensities of the Raman bands for the lighter and darker strands as shown in Figure 4.

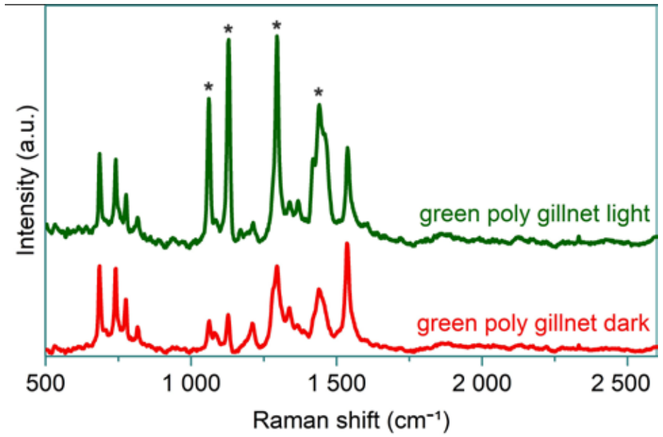

Figure 4: Baseline corrected spectra of light (top) and dark (bottom) colored strands from the green polytwine gillnet sample. The asterisks indicate bands of significantly differing intensity between the two measurements.

Using HORIBA's LabSpec 6 software suite, the spectrum recorded from the darker colored strand was subtracted from the lighter colored strand and vice versa. The subtracted results revealed spectra that closely matched with polyethylene (light – dark) and pigmosol green (dark – light) as shown in Figure 5 and Figure 6, respectively. In this unknown sample, the polytwine gillnet was not nylon at all, but polyethylene. Despite significant spectral contributions from the pigment, the polymer could easily and confidently be identified.

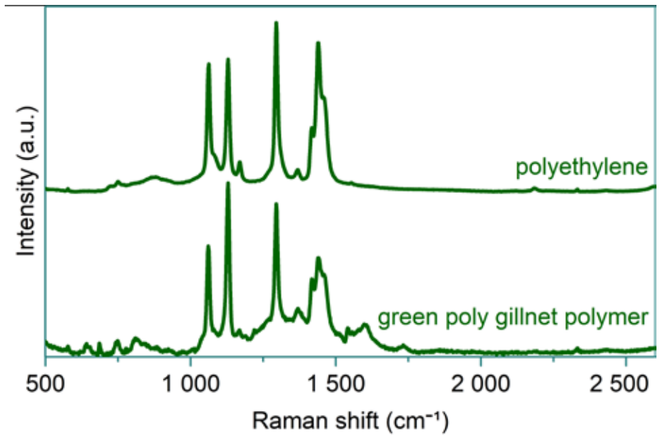

Figure 5: Reference spectrum of polyethylene (top) and subtracted spectrum of the light strand from the green polytwine gillnet sample (bottom).

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Raman polymer identification of fishing gear using Raman spectroscopy, cont.

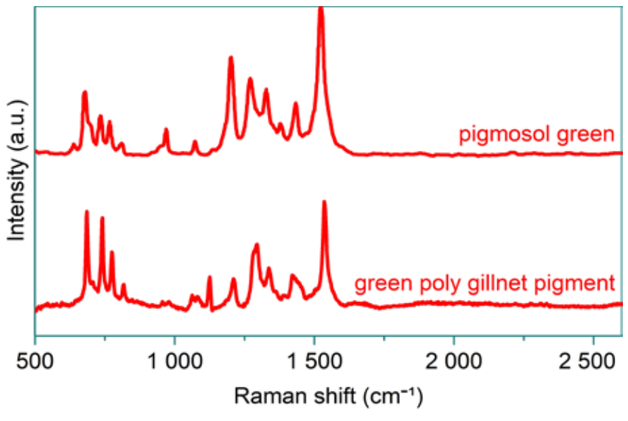

Figure 6: Reference spectrum of pigmosol green from Wiley's KnowItAll software and spectral libraries (top) and subtracted spectrum of the dark strand from the green polytwine gillnet sample (bottom).

While these measurements were performed in a laboratory environment, the results suggest that the MacroRAM could also easily be deployed for field measurements at the site of collection for abandoned nets. Identification can be carried out easily and quickly in real time while sorting through fishing gear, and bundling it for shipping using a remote touch probe. In addition, advanced data processing capabilities in LabSpec 6 enable more complex post-acquisition analysis that could not be carried out with simpler handheld Raman devices. Especially for samples with large spectral contributions from pigments, this allows for unambiguous determination of the polymer type.

Lastly, these results are also promising for the measure- ment of microplastics in a rapid, alignment-free manner. The unknown fiber samples measured in this study ranged in size from 260 µm to 920 µm in diameter. This is well within the range of the definition of microplastics (< 5 mm). Microplastic samples in the range greater than 100 µm in size are routinely hand-picked for observation using a stereo microscope. The addition of a benchtop Raman system coupled to a remote touch probe would provide rapid chemical identification at the point of microplastics sorting and classifying (in size, morphology, and color). The next advancement would be to deploy the unit in the field to measure microplastics at the source, for example on a coastline or a boat.

Conclusion

The MacroRAM benchtop Raman spectrometer coupled with a remote touch probe provides easy, accurate identification of polymer type from a variety of colored fishing nets. There is not only clear distinction among different polymer classes (polyethylene and nylon) but also within a single polymer class (nylon 6 and nylon 6,6). The methods demonstrated here could be easily expanded for field measurements at the site of abandoned fishing gear or for measurements of microplastics at the source.

Acknowledgements

Thank you to Kayla Brignac and Jennifer Lynch of Hawaii Pacific University and Nicole Baker of *Net Your Problem* for supplying HORIBA with the samples used in this study.

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HORIBA Scientific in Europe contributes to the harmonization of analytical methods in the field of microplastics research.

A focus on HORIBA European network activity around microplastics

Current research on microplastics, ranging from discovering or confirming their presence in various environments, to quantifying their induced pollution in food matrices, to understanding their impact on wildlife, ecosystems and even human health has become a hot topic worldwide. Europe has always been attentive to environmental issues and prompt to sponsor coordinated programs at the academic level, but also to regulate the different industries whose activities may generate microplastics. This featured article will detail a few initiatives from HORIBA Scientific in Europe to contribute to the harmonization of analytical methods, including sample collection and preparation, as well as to the development and validation of standard reference samples in the field of microplastics research.

Microplastics (MPs) are present in every environmental compartment, including in the remotest places on earth, and have gained recent interest as a major environmental pollutant. In 2015, the European Union (EU) produced 25 million tons of plastic waste, with 60% still originating from packaging, representing an average of 31 kg per person per year. Worth noting is the fact that the majority of the MPs released in the ocean originate from synthetic textiles, tire dust or city dust.

“Plastic” is not a well-defined term, but rather encompasses a set of synthetic polymeric materials having a wide range of high molecular weight, and whose particle dimensions span 6 orders of magnitude in size, from the nanometer up to 5 mm. MPs present a large variety of chemical compositions: (co)polymers, residual monomers, chemical additives, catalysts or fillers, and can even be contaminated by non-intentionally added substances. While naturally occurring polymers exist, such as rubber or cotton, plastic pollution mostly originates from a few synthetic polymeric families like polystyrene (PS), polyethylene (PE), polypropylene (PP), polyvinylchloride (PVC) or polyethylene terephthalate (PET).

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A focus on HORIBA European network activity around microplastics, cont.

This diversity gave rise to a search of a variety of methodologies to answer the burning questions in MPs research and, to support plastic pollution monitoring and mitigation policies under consideration by state and non-state actors. The existence of various definitions for different regulatory sectors and regions also complicates understanding and implementation of legislation.

Moreover, no validated and harmonized standard methods are currently available for the analysis of MPs, and many analytical protocols and techniques are used. There is still no consensus on the reporting format, in terms of number of particles, mass of size fractions, and an absence of certified reference materials to investigate analytical proficiencies. Those points were highlighted during the Global Summit on Regulatory Science (GSRS) 2019 Nanotechnology and Nanoplastics, which took place in Ispra (Italy) in September 2019,[1] organized by the European Commission Joint Research Center (JRC), whose mission is to provide scientific advice and support to the European Union policy.

All this explains why open inter-laboratory studies were recently set up in order to address those shortcomings.

Evidence of microplastics in food

HORIBA Scientific is proud to count world-leading research teams among our customers of Raman spectrometers. Their affiliations reveal the wide range of fields where Raman microscopy is used to study MPs: Environment institutes, health and food safety authorities, oceanology and hydrology departments, marine biology agencies, ecotoxicology laboratories, but also water treatment and distribution entities or bottled water companies.

Clearly, the most pressing question on the scientific community agenda is whether or not MPs pose a threat to human health, especially through seafood consumption. To that extent, the European Food Safety Authority (EFSA) Panel for Contaminants in the Food Chain (CONTAM) was asked, following a request from the German Federal Institute for Risk Assessment (BfR), to deliver a statement on the presence of MPs (but also nanoplastics) in food, with particular focus on seafood.[2]

This bibliographic review confirmed that MPs can be ingested by many marine invertebrates and have the potential to be transferred between trophic levels, as illustrated in Figure 1. Indeed, the presence of plastic debris, indicated as anthropogenic debris, in the gastrointestinal tract of fished on sale for human consumption was sampled from markets in several countries.

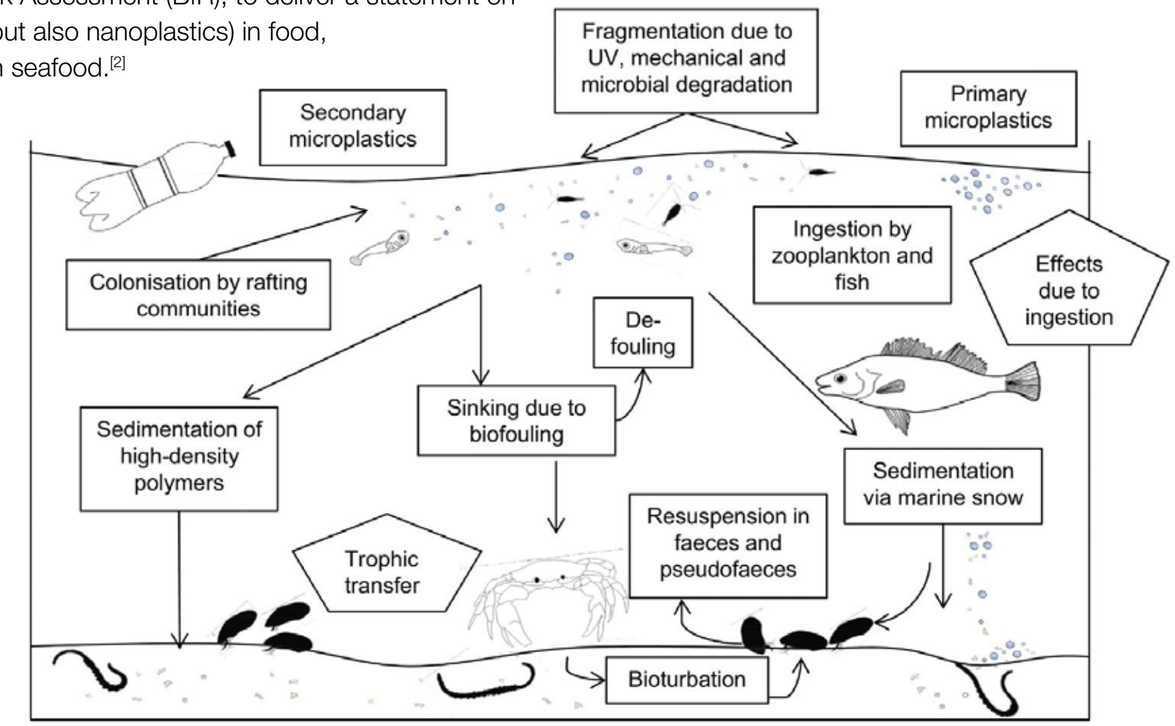

Figure 1: Potential pathways for the transport of microplastics and their biological interactions.[1]

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A focus on HORIBA European network activity around microplastics, cont.

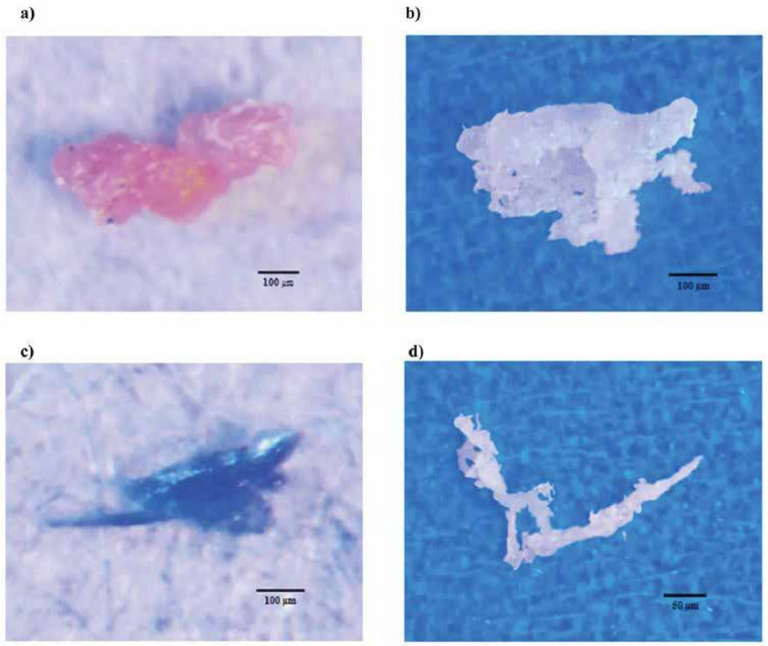
Following on this statement, a team of researchers from IFREMER (French Research Institute for Exploitation of the Sea) and ANSES (French Agency for Food, Environmental and Occupational Health & Safety) has developed a protocol to extract and characterize MPs from seafood tissues, which should be implemented to assure the relevance and comparison of further studies, or assess seafood product quality, notably to follow recommendation from the OSPAR Convention for the Protection of the Marine Environment of the North-East Atlantic, ratified by 15 EU countries in relation with the Marine Strategy Framework Directive.

Plastic integrity and composition was evaluated through microscopic inspection with the use of HORIBA LabRAM Raman spectrometer, before and after digestion by KOH 10% solution with 24 h incubation at 60°C.[3]

Again, related to fish meal pollution, HORIBA Scientific recently participated in a study which demonstrated that cultured (farmed) organisms could be exposed to high levels of MPs via contaminated fish/shellfish used in fish meal production by the aquaculture industry.[4] The most abundant isolated plastic polymer was PE (63.0%) followed by PP (27.8%) and PET (8.8%), while the average size of the particles was found to be 855 µm.

Another publication coauthored by HORIBA Scientific in Scientific Reports[5], made the headlines when it revealed the presence of MPs even in commercial sea and lake salts originating from 8 different countries (Figure 2). This study also raised concerns over the possible transfer of other contaminants associated with MPs into salt, such as pigment fragments, some of them being toxic.

Another milestone article investigated the presence of MPs in mineral waters from different bottle types.[6] Led by scientists from the Bavarian Health and Food Safety Authority (LGL) in Germany, the team focused on small particles (below 5 µm) posing higher toxicological risks, as they have the potential to translocate into body tissues and are more likely to penetrate deeply into organs.



Using a HORIBA XploRA PLUS system to locate and identify particles down to a size of 1 µm on specially prepared aluminum coated olycarbonatemembrane filters, evidence of higher amounts of MPs in reusable bottles (PET as well as glass) was found compared to single use bottles.

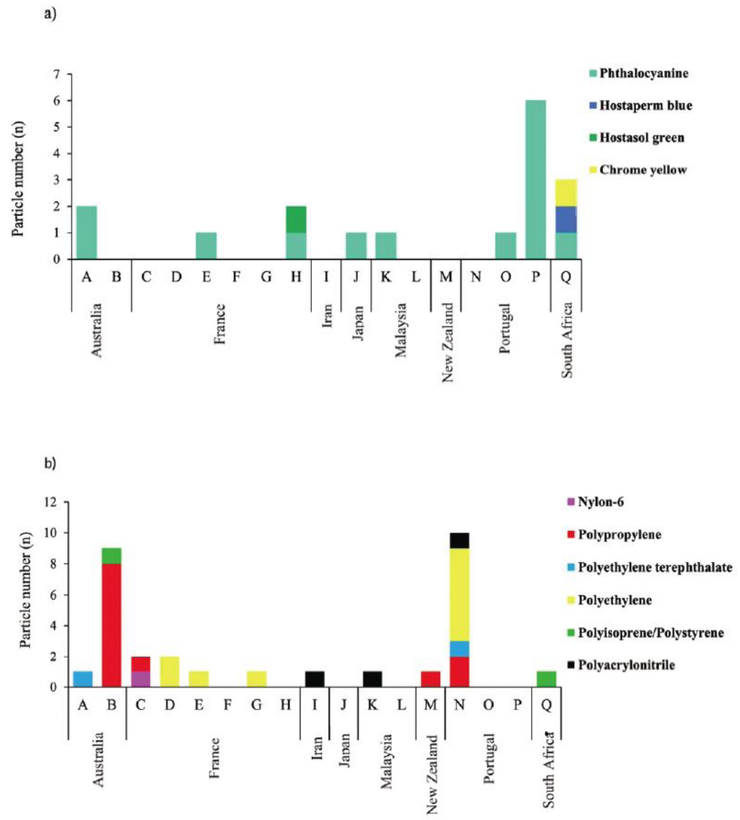


Figure 2: (Left) Microscopic images of some of the extracted particles. (a) polyisoprene/polystyrene, (b) polyethylene, and (c) pigment (phthalocyanine) fragment. Image (d) is a nylon-6 filament. (Right) Stacked bar chart of the number of (a) plastic polymer and (b) pigment particles isolated from different salt brands.[5]

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Open interlaboratory studies

A recent meeting hosted by the Group of Chief Scientific Advisors of the European commission[7], supported by the evidence review of the SAPEA Consortium (Science Advice for Policy by European Academies)[8], concluded on the lack of harmonized methodologies in order to generate standardized data. On this basis, several organizations initiated collaborative programs with the aim of validating internal laboratories, quality assessment and competence, supporting environmental data, providing data for national and international stakeholders or supporting accreditation.

One of the initiatives in which HORIBA took part was set up by the Vrije Universiteit Amsterdam (VUA), the Norwegian Institute for Water Research (NIVA) and the WEPAL (Wageningen Evaluating Programmes for Analytical Laboratories) organization based in the Netherland and recognized by the Dutch Accreditation Council (RvA).

This international interlaboratory study on MPs, called QUASIMEME for “Quality Assurance of Information in Marine Environmental Monitoring”, saw 34 laboratories participating to analyze the test materials between May and August 2019, using several instrumental and quantification methods, with the objective of counting the particles and identifying their chemical family.

Test samples were prepared at NIVA, to enable the analysis by a broad variety of analytical methods and techniques: Visual, hyperspectral imaging, Fourier transform Infrared Spectroscopy (FT-IR), Raman and Mass Spectrometry ; and consisted of 6 preproduction pellets, 5 tablets containing microplastics fragments (obtained after filtration of PET, PVC and PS powder) of fibres and 1 blank tablet. The fibres were created by washing polyester blankets in a typical domestic washing machine. While the majority of the participating laboratories used ATR-FT-IR (Attenuated Total Reflection FT-IR) or µ-FT-IR, we employed Raman microscopy (Figure 3), which is favorable for small size particles, typically below 20 µm]

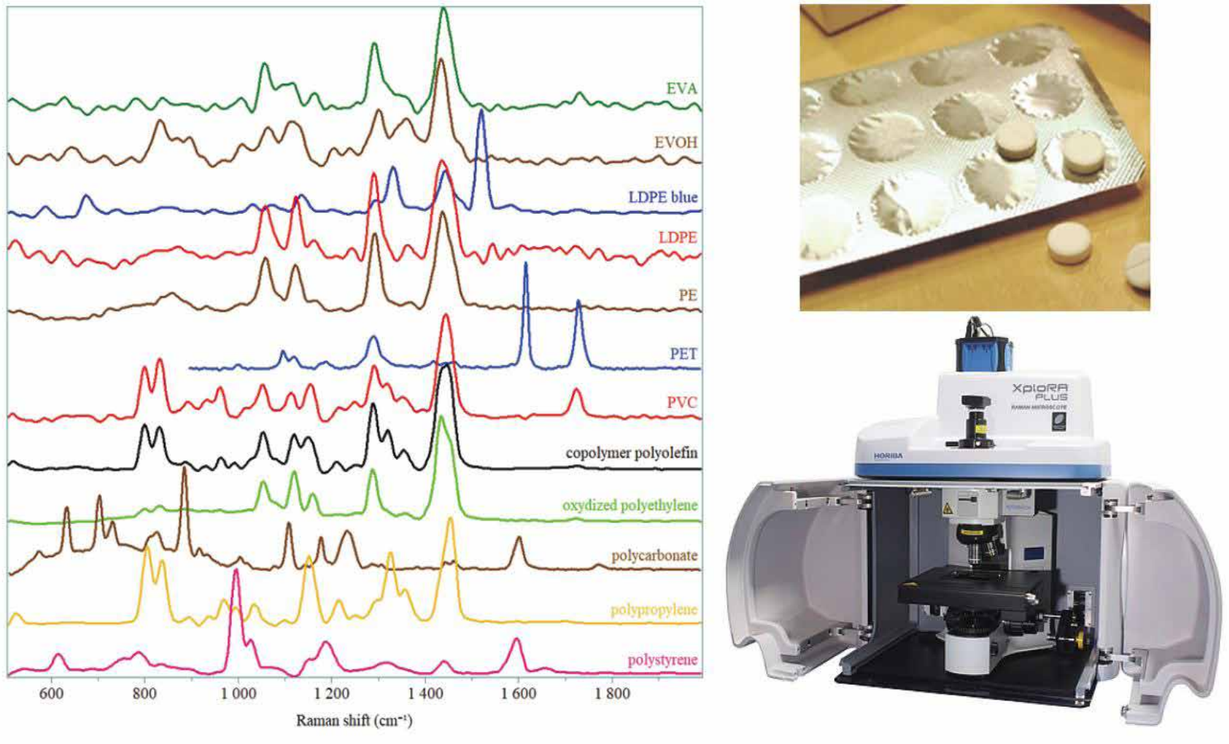

Figure 3: (Left) Raman spectra recorded on different polymer families. (Top right) Aluminum strip pellet containing 12 tablets sent to participants, that were to be dissolved in analytical grade water to control background contamination. (Bottom right) HORIBA Xplora PLUS Raman microscope with class I laser enclosure used for this study.

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Table 1 shows an example of a reported table by the participants for one of the tablet samples. Although some polymer misidentification occurred in some cases, the polymer type was correctly assigned for both larger preproduction pellets (2-4 mm) and particles or fibres added to the tablets (150-300 µm). However, the reported number of particles varied considerably (up to 78% standard deviation), and the standard deviations of the determination of the polymer type in the tablets varied from 29% (for PET) to 99% (for PS).

Overall, the results of this first round indicate that polymer identification and quantification of the number of plastics particles in a sample (especially in smaller size fractions) is not simple or straightforward. Yet, HORIBA's Applications Laboratory was able to demonstrate analytical results on par with recognized European facilities.

This round of the QUASIMEME study will be followed by exercises with increasing complexity and difficulty of samples, including MPs extracted from complex matrices (e.g. sediments and fishes). After several study rounds, the analytical methodologies for MPs are expected to be better comparable and will be included in a routine proficiency testing scheme.

HORIBA Scientific also recently responded to a call to enter an exploratory study organized by the JRC, with support from the German Federal Institute for Materials Research and Testing (BAM).[9] The aim of this proficiency test study on MPs in water in sediments is to help in the identification of possible method candidates for future validation and standardization.

In practice, reference samples employed to benchmark laboratories were developed and qualified beforehand. Those samples were sent to the different laboratories to be prepared on site through a reconstitution protocol, from vials containing a NaCl-carrier with embedded PET particles, a surfactant solution (triton X-100), and deionized water. Participants are to report the number of particles or mass of particles above 30 µm, the particles identified as PET, particles identified as plastic (including PET) and particles of any kind, with a report of the measurement uncertainty.

A workshop will take place during the summer of 2020 to discuss the results and conclusions once the participants report their findings.

Laboratory	acrylonitrile butadiene styrene	Black fiber	Blue fiber	Cellulose	Cellulose fiber black	Cellulose fiber white	Crystaline particles	Grey fiber	Grey piece	High density polyethylene	Low-density polyethylene	polymethylmethacrylate	Polyamide	polybutylmethacrylate	Polycarbonate	Polyester	Polyethylene	polyethylene terephthalate	Polypropylene	Polystyrene	Polytetrafluoroethylene	Polyurethane	Polyvinylchloride	red fiber	TIO2	Unknown	Total particles
H221																44											44
Q101				8														5	< 3	8			14				35
Q104					1	85												9		13			18				126
Q110																		3								4	7
Q114																		2								28	30
Q134											1							7	1	26			26				61
Q152																							34			3	37
Q153																										48	48
Q871																		7	2	37							46
Q968		2						1	1																		4
Q3175			3			6														10				2			21
Q3231																8				13						19	40
Q3239																											
Q3872																	8	11		33			21				73
Q3873	1											1					30		8	39							79
Q3876																				5			10				15
Q3877																											
Q3878																		31		22							53
Q3879																		5	5	6			17				33
Q3882																				11			30				41
Q3883																8				17			19				44
Q3884																				28			27				55
Q3885																		1		6			20				27
Q3887																		7		23			26				56
Q3888	1										8			1				10	6	51	2	1	10				90
Q3889							17			7																	24
Q3890												1						3		29			32				65
Q3891															30			6		12			14	3			65
Q3892																		3		2			11				16
Q3894																											
No. of reporting labs	2	1	1	1	1	2	1	1	1	1	2	1	1	1	1	3	2	15	6	20	1	1	16	1	1	5	27
Average	*1*	*2*	*3*	*8*	*1*	*46*	*17*	*1*	*1*	*7*	*4.5*	*1*	*1*	*1*	*30*	*20*	*19*	**5.5**	**4.4**	**17.1**	*2*	*1*	**20.2**	*2*	*3*	**18.5**	**42.0**
Standard deviation						*56*					*4.9*					*21*	*16*	4.0	3.9	13.3			9.25			20.9	24.3

Table 1: Type and number of plastic particles reported for table in position no. 10 in the strip pellet shown in Figure 3, by all the participating laboratories of the QUASIMEME study.

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A focus on HORIBA European network activity around microplastics, cont.

References

Finally, HORIBA France is actively involved in a group of experts within the French Standardization Association (AFNOR) currently working on establishing a regulation on the analysis of MPs in drinking water, through spectroscopic techniques (µFT-IR and Raman). This group, part of the T91M “Organic micropollutants” Commission, gathers various governmental, academic and industry organizations, including the Standardization Bureau for Plastics and Plastics Engineering (BNPP), with the objective of drawing up a new norm for the first half of 2021. This work was presented at the last ISO (International Organization for Standardization) meeting held by the Technical Committee TC 147 on Water Quality in Tokyo, with the purpose of reaching a global consensus in the near future.

Challenge and perspectives

With the improvement of the robustness of analytical techniques, researchers working in the field of MPs will more easily be able to trust their results and compare their studies. The most pressing question to answer, as little is known at this point, concerns the toxicity of MPs on human health. In particular, an important aspect revolves around the fact that MPs both absorb and give off toxic chemicals and harmful pollutants, which may build up over time and stay in the environment. There is also a clear lack of knowledge on nanoplastics (particles smaller than 0.1 µm), which may represent a greater risk to the environment and health. However, their characterization is currently hindered by technical limitations and will require new instrumental developments.

* This content is based on our investigation at the year of issue unless otherwise stated.

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HORIBA Group engineers and scientists in Japan are working to establish measurement techniques for microplastics analysis.

Microplastics – related activities in our HORIBA Group, Japan

In recent years, plastics pollution has become a widely discussed international problem. Drifting into the ocean from the urban areas, plastics gradually miniaturize into small particles called microplastics, that affect ecosystems in many ways. HORIBA Group engineers and scientists in Japan and worldwide, are working to establish the measurement techniques for microplastics analysis. In this paper, we will introduce our HORIBA Group's efforts in Japan, in response to the microplastics analysis needs, including application examples.

In the past several decades, plastics were widely used due to their many convenient benefits, but in recent years, the plastic pollution has become a widely discussed international problem. Drifting into the ocean from the urban areas, plastics gradually miniaturize into small particles that affect ecosystems in many ways. These plastic particles are called Microplastics (MPs) when they get smaller than 5 mm.

The G20 summit held in Osaka in June 2019, resulted in the "Osaka Blue Ocean Vision" declaration which aims to stop any additional pollution being introduced into the ocean by 2050. To achieve this goal, the Japanese "Ministry of the Environment" and "Ministry of Economy, Trade and Industry" has introduced several programs: (1) reduction and replacement with alternative materials, (2) recycling and resource circulation, (3) countermeasures against sea pollution, and (4) introduction of various national movements for dissemination and awareness activities.

Analytical instruments for MPs characterization

MPs size range and evaluation parameters depend on analysis purposes and survey targets: Sea, river, lake, pond, sewage treated water or factory drainage. Measurement conditions and the applied instruments are shown in Table 1.

Survey target	MPs size	Preparation	Analytical instruments
Sea, River, Lake and Pond	300 µm ~ 5 mm	Picking up	FT-IR, Raman pyrolysis-GCMS
Sewage water, Factory drainage	10 µm ~ 300 µm	Primary filtration ↓ Oxidization ↓ Gravity separation ↓ Secondary filtration	FT-IR Microscope Raman Microscope
Clean water, Drinking water	< 10 µm		Raman Microscope
Food Cosmetic			
Impact on Ecosystem (biocells)			

Table 1: Survey target, condition and applied instruments for MPs identification

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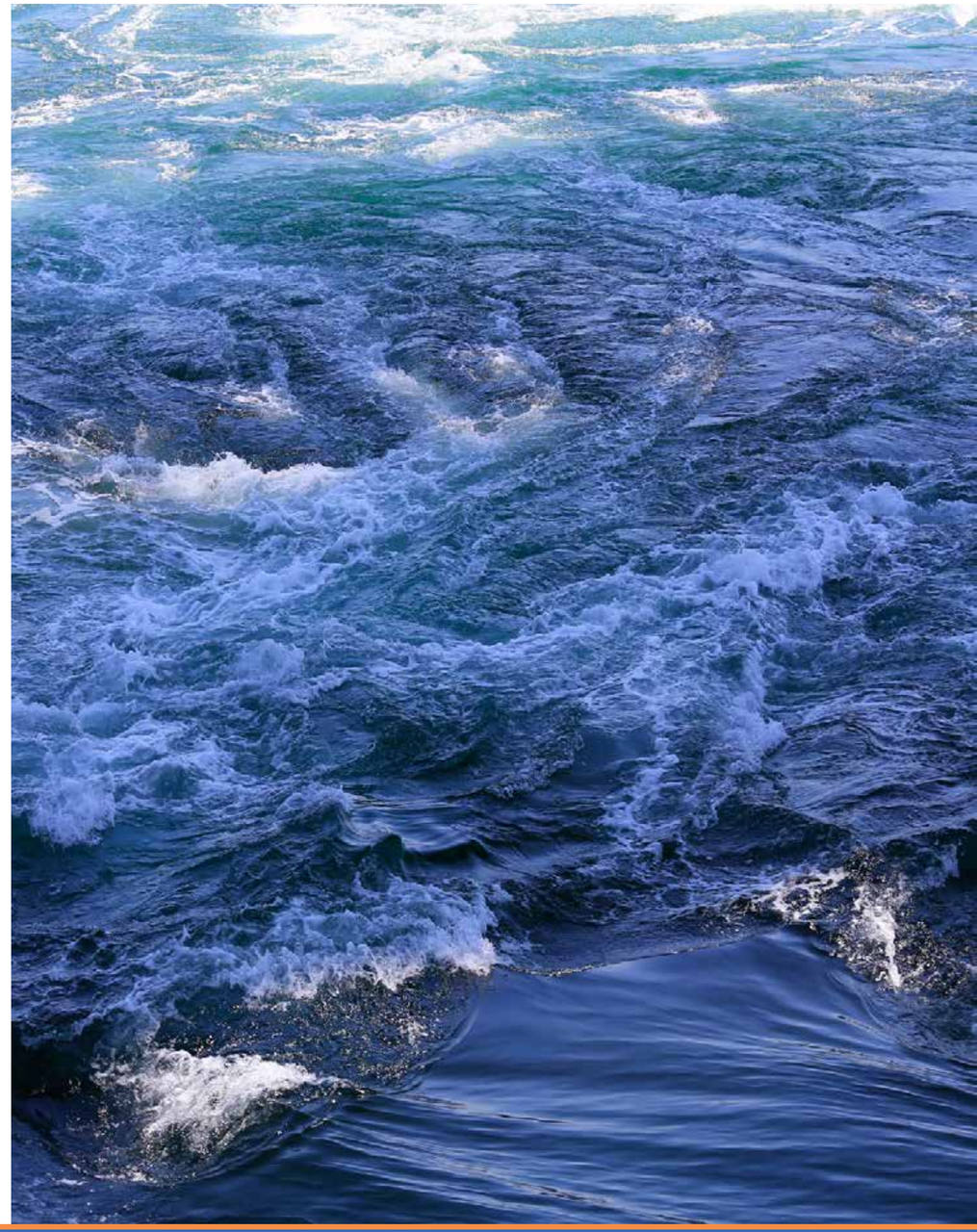

Microplastics – related activities in our HORIBA Group, Japan, cont.

MPs measurement's issues In the case of MPs characterization, analytical methods and measurement parameters, depend on the evaluation target: Particle size, composition, mass, surface area, and identification of plastic types and additional hazardous substances. Furthermore, the method of collecting the sample, the method of removing contaminants and pretreatment differ depending on the target sample. The smaller the MP's particle size, the more difficult characterization becomes. Many of above mentioned methods are currently performed using each researcher's personal knowledge. This now needs to be considered towards a standardization process for better reproducibility of research and for reliable data comparison moving forward. Currently it also requires a lot of time and effort to perform multiple measurements, because most of sample treatments are done manually. Therefore, automation and semi-automation for sample treatment should be prioritized to reduce signifi cantly the time and labor required for MPs analysis.

Activities in Japan

As a reaction to the MPs pollution problem, many seminars and symposiums have been held in Japan's industry and academia societies. In various seminars, on the theme "Particle size analysis and Raman spectroscopy for MPs," HORIBA has introduced measurement examples using HORIBA products. Several instruments like: The Laser Diffraction Analyzer (LA-960V2), the Dynamic Laser Scattering (SZ-100V2) and the Nanoparticle Tracking Analyzer (ViewSizer™ 3000), are used to characterize particle size and distribution, particle number and concentration, zeta potential and aggregation conditions. Our capability to cover a wide size range of samples (mm ~ µm ~ nm) was introduced.

In addition, we have demonstrated that our Raman microscopes (XploRA PLUS and LabRAM Evolution) equipped with the particle analysis function (Particle-Finder) enables users to associate chemical information with particle size, shape, number and compositions using automated image analysis functions for the component analysis, performed using Fourier detection and positioning of small particles.

A list of events and presentation titles are summarized in Table 2 and HORIBA product pictures, used for this study, are shown in Figure 1.

MPs mock sample analysis

The presence of MPs in our environment other than environmental water, such as our ocean and rivers, has also been reported, for example in air, drinking water and food.[2] In this article, we will introduce two analysis examples: Mock MPs samples from environmental water and MPs obtained from the atmosphere.

A MPs mock sample was prepared by pulverizing a polypropylene (PP), polyurethane (PU), polymethylmethacrylate (PMMA), and polyethylene terephthalate (PET) mixture.

Component analysis was performed using Fourier Transform Infrared (FT-IR) microscopy. Particle size distribution and image observation were performed using a laser diffraction/scattering particle size analyzer with an optional built-in Imaging Unit.[3] The respective measurement systems will be described below.

Event name	Date	Title	Organizer
JASIS conference	2019/9/6	Microplastic measurement and environmental impact	Japan Society for Environmental Chemistry (JSE) Japan Analytical Instruments Manufacturers' Association (JAIMA)
JETA seminar	2019/11/28	Measurement of microplastics in environmental water	Japan Environmental Technology Association (JETA)
AIST symposium	2019/12/2	Measurement and evaluation of microplastics	National Institute of Advanced Industrial Science and Technology (AIST)

Table 2: List of events and presentation title

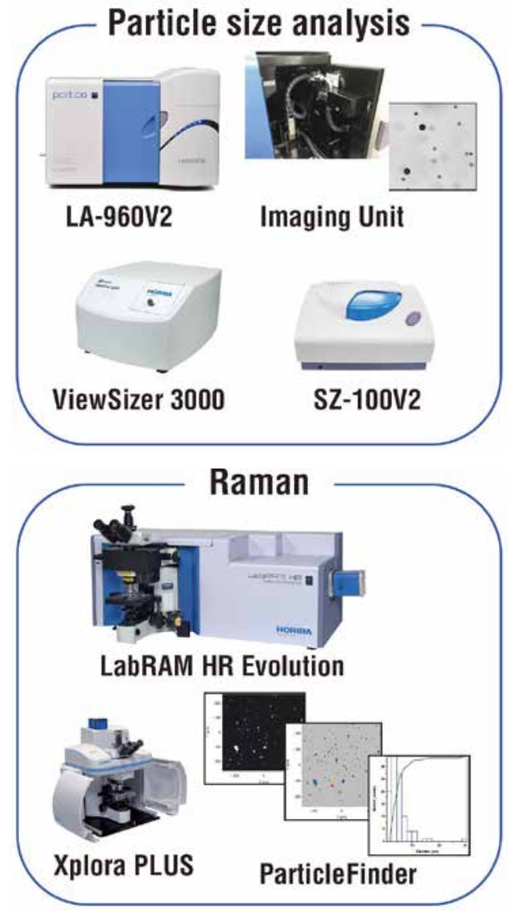

Figure 1:
HORIBA product's pictures,
used for this study

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Microplastics – related activities in our HORIBA Group, Japan, cont.

In infrared spectroscopic analysis, when a sample is irradiated with infrared light, an infrared absorption spectrum is obtained from an absorption value at each wavelength. A component analysis is performed using this infrared absorption spectrum. FT-IR microscopes use focused infrared light with a spatial resolution of about 10 µm. When combined with a motorized stage it is capable of obtaining component infrared spectral images of a wide area.

The laser diffraction/scattering particle size analyzer can measure the particle size distribution of a sample. When the sample is irradiated with incident light at certain wavelengths, the scattered light angular distribution intensity changes according to the particles' diameter size. By analyzing this pattern, the particle size distribution in the sample can be obtained. The sample dispersed in the liquid circulates in the flow cell. Since many particles are measured at the level of several millions, statistically high accuracy and measurement reproducibility can be obtained compared with the counting method using a microscope. Figure 2 shows the optical set up for the laser diffraction/scattering particle size analyzer.

The Imaging Unit is an optional built-in unit used for image analysis. White light is emitted into the back surface of the cell, from a light source installed in the Imaging Unit, and a transmission image of particles in the cell is captured by a strobe camera.

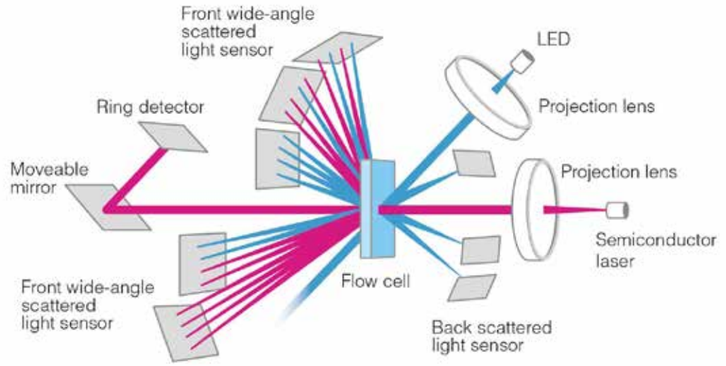

Figure 2: Optical set up of a laser diffraction/scattering particle size analyzer distribution measurement device

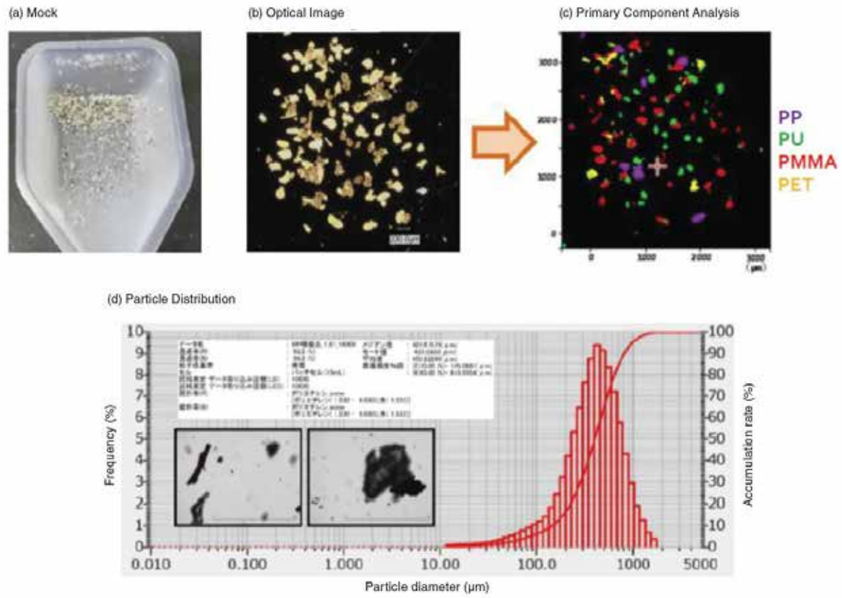

Figure 3: Optical image and measurement results of MPs mock sample
*Figure 3 kindly provided by Toray Research Center, Inc.

Particles in this circulated flow cell can be observed in real time, and a histogram of particle size distribution can be calculated from image particle analysis results. Histogram of particle size distribution can be calculated from image particle analysis results.

After collecting water from the ocean or river, and pretreatment for MPs separation, the measurement of particles number and a component analysis by FT-IR microscopy is widely adopted for the MPs analysis. The MPs mock samples used in this study were prepared by pulverizing a PP, PU, PMMA, and PET mixture. A photograph of the sample inside the plastic case is shown in Figure 3(a). This sample was dispersed on a metal substrate and infrared refl ection-absorption imaging was performed by a FT-IR microscope. The spectrum obtained from each measurement point was subjected to principal component analysis to obtain a distribution chart of PP, PU, PMMA and PET. As shown in the Figure 3(b), (c), all the particles in the observed image could be identified.

The laser diffraction scattering particle size analyzer used for the same mock sample found the particle size distribution to be within a 10 µm to 2 mm range. As shown in Figure 3(d), it can be seen that the results can be obtained with high particle size resolution. Inserted in part of Figure 3(d) shows images of particles with different shapes . Using the Imaging Unit, it is possible to observe actual particles simultaneously with the particle size distribution.

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Microplastics – related activities in our HORIBA Group, Japan, cont.

Measurement of Airborne Microplastics by Raman Microscopy

Currently several researchers have reported airborne microplastics (AMPs) found in the atmosphere of urban areas, high altitude mountains and the arctic circle.[4] These facts suggest that AMPs contamination is widely spread due to atmospheric circulation. In addition, AMPs smaller than 10 μ may have a bad infl uence not only on the environment, but on human health due to inhalation.[5]

In this study, we evaluated AMPs collected in the free troposphere (ca. 2000-11000 m a.s.l.) by researchers in Waseda University. AMPs collection was performed at night on the top of Mt. Fuji at an altitude of 3776 m. A cyclone type High Volume Air Sampler (Sibata Scientific Technology Ltd.) was used to collect PM2.5 particles on a Teflon filter. Chemical composition analysis was performed after removing natural organic or inorganic particles. In general, a FT-IR microscope is used to analyze larger microplastics, but because the expected estimated size of AMPs is smaller than 10 μm, the FT-IR microscope spatial resolution would be not sufficient. Therefore we decided to use Raman microscopy
which has a much higher, up to sub-micron scale, spatial resolution.

Raman spectroscopy can perform composition analysis and crystallinity evaluation from inelastic light scattered (Raman scattering) on a laser irradiated sample. By combination of a microscope and motorized sample stage, sub-micron spatial resolution Raman chemical imaging is achievable.

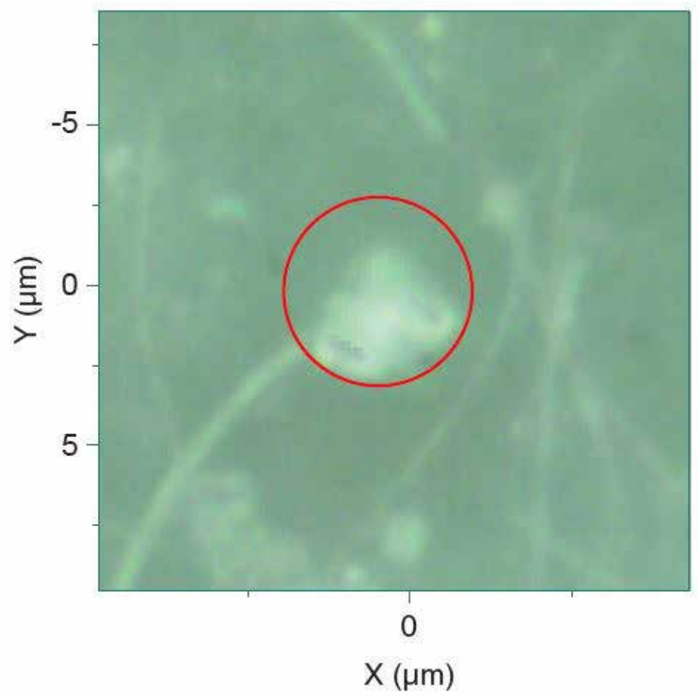

Figure 4: Optical image of detected AMPs

Figure 5: Image of CH stretching mode intensity

In order to perform Raman measurements, we transferred AMPs to an Almina fi lter and carried out mapping measurement in 4 areas, 1 mm^2 each, followed by the imaging of CH stretching mode intensities. This image illustrates distribution of the existing organic compounds in the AMPs. 30 pieces of AMPs were detected in the 4 mapping areas.

By conducting point measurement of detected AMPs with longer acquisition times, a total of 15 different polymer species where identified. Figure 4 shows the optical image of part of the detected AMPs on the Almina fi lter using a X100 objective lens. Figure 5 shows the image of CH stretching mode intensities in one of the mapped areas.

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Microplastics – related activities in our HORIBA Group, Japan, cont.

target	Size/µm	identified compound by Library search
1	8 (diameter)	Polystyrene (PS)
2	6 (Maj axis), 4 (Min axis)	Unidentified polymer + TiO_2
3	3 (diameter)	Polyester
4	4 (diameter)	Polypropylene (PP)
5	6 (Maj axis), 4 (Min axis)	Polyurethane (PU)
6	12 (Maj axis), 3 (Min axis)	Polyethylene (PE)
7	1.4 (diameter)	Poly-3-Hydroxyl Butyl acid
8	2 (diameter)	Polyolefin
9	28 (Maj axis), 2 (Min axis)	Palytetrafluoro ethylene (PTFE)
10	ND	Polyolefin

Table 3: AMPs size and identified species chemical names

In Table 3 the AMPs size and identified species chemical names are summarized. Most of the AMPs were smaller than 10 µm. 37% of detected particles were made from Polypropylene material, followed by biodegradable plastics such as Polyhydroxybutyric acid.

The AMPs number concentration in the atmosphere, calculated in this study, was found to be 4.47 particles/m^3. These results show that Raman microscopy is suitable for the qualitative analysis of MPs composition for particles smaller than 10 µm.

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Acknowledgments

We would like to thank Mr. Takemoto of Toray Research Center, Inc., for providing us application data for the MPs mock sample analysis. We would like also to thank Prof. Hiroshi Okochi of Waseda University, Faculty of Science and Engineering, for providing samples and guidance for AMPs analysis.

* This content is based on our investigation at the year of issue unless otherwise stated.

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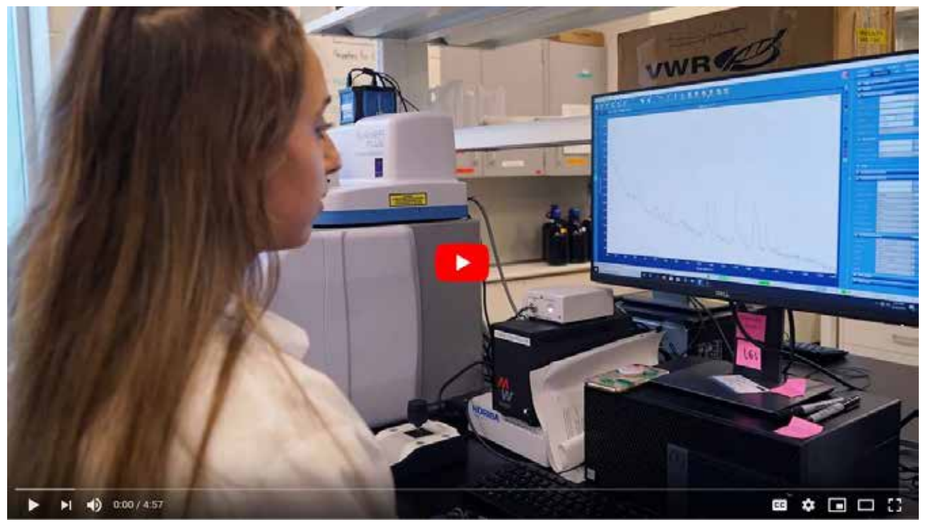
Videos & Webinars

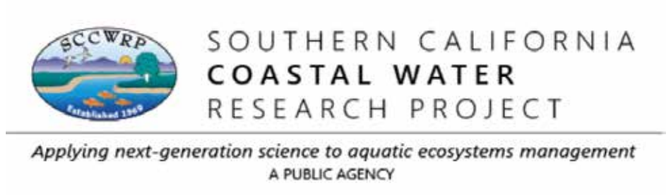
Microplastics explained



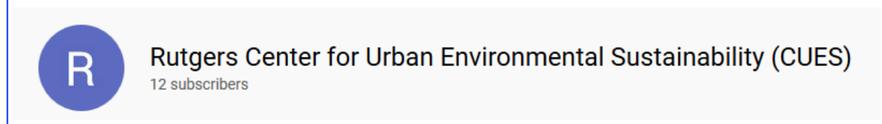
Analyzing microplastics

This webinar describes the use of Raman spectroscopy for the characterization of microplastics and nanoplastics (plastic particulates < 5 mm), which threaten the environment and potentially human health. An overview of the process of microplastic characterization will be given including a discussion of collection, extraction, detection, and identification methods, with a view to support future legislation and monitoring of microplastic contamination. The necessary high throughput requirements of microplastics analysis will also be addressed through automation of Raman spectral measurements of large quantities of microplastics.

Resources



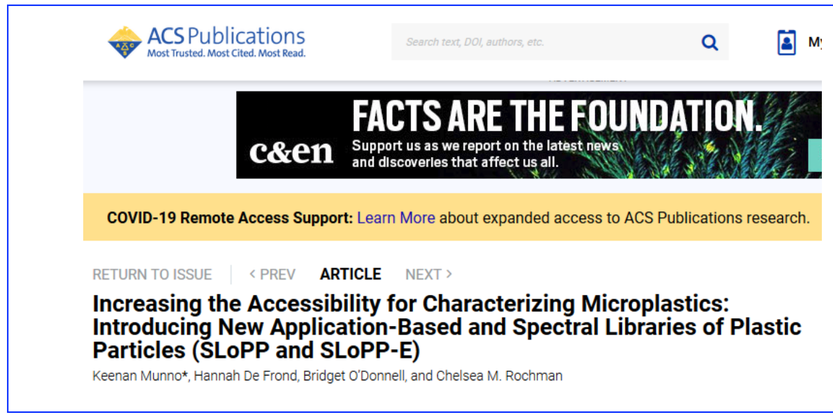
Measuring Microplastics Workshop
Southern California Coastal Water Research Project (SCCWRP)



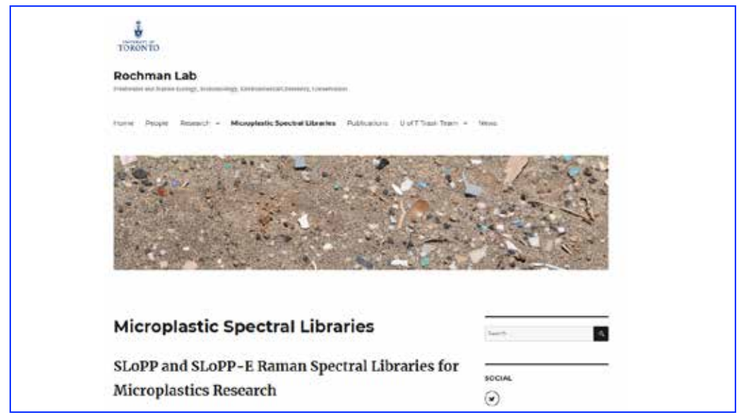
Impacts of Microplastics in the Urban Environment Conference
Rutgers Center for Urban Environmental Sustainability

Applied Spectroscopy (Magazine) Special Issue: Microplastics

"*Characterizing Microplastic Fibers Using Raman Spectroscopy*"
Spectroscopy (Magazine)



"*Increasing the Accessibility for Characterizing Microplastics: Introducing New Application-Based and Spectral Libraries of Plastic Particles (SLoPP and SLoPP-E)*"
Analytical Chemistry (Magazine)



SLOPP and SLOPP-E Raman Spectral Libraries
for Microplastics Research

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