Helping solve the rubik's cube plastic problem

Bonnie Monteleone
Executive Director
Plastic Ocean Project
UNCW Plastic Marine Debris Research

E. R. Zettler, H. Takada, B. Monteleone, N. Mallos, M. Eriksen, and L. A. Amaral-Zettler, *Incorporating citizen science to study plastics in the environment,* Analytical Methods, Royal Society of Chemistry, 2017.

Research team

Special thank you to:

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- Pam Seaton, PhD.
- John Tyrell, PhD.

Intersection between:
socio-economic systems

1. Saves lives
2. creates jobs
3. lightweight, shatterproof, versatile, and inexpensive

And Nature

1. Chemical properties pose potential heath risks
2. Marine life ingest plastics
3. Creates navigational hazard for humans and marine life
4. Transports invasive species
5. Smothers benthic ecosystems

What makes plastics versatile?

the additives

- Alkylphenols – plastic stabilizer
- Bisphenol A (BPA) shatter-resistant, enhances plastic clarity
- Phthalates –Plasticizer (making plastics flexible and pliable)
- Polybrominated diphenyl ethers (PBDEs) flame retardants

Negative Externalities and Governances

All are known to leach from the plastic products, are endocrine disruptors (estrogenic properties), and are suspect to side effects in human health and the environment. (Halden, 2010)

[Banning BPA]

Polychlorinated biphenyls (PCBs) massed produced in 1929, health effects began to be evident 1936, banned in 1977.

***Chemicals are innocent until proven guilty**

Example (PPB= 1pancake of a stack 4K miles high)

The NuvaRing is clinically effective at 0.035 parts per billion and 99% effective at preventing pregnancy

According to the American Academy of Pediatrics children are far more affected by:

Chemical Bisphenols
Phthalates
Perfluoroalkyl chemicals (PFCs)
Perchlorate Nitrates and nitrites

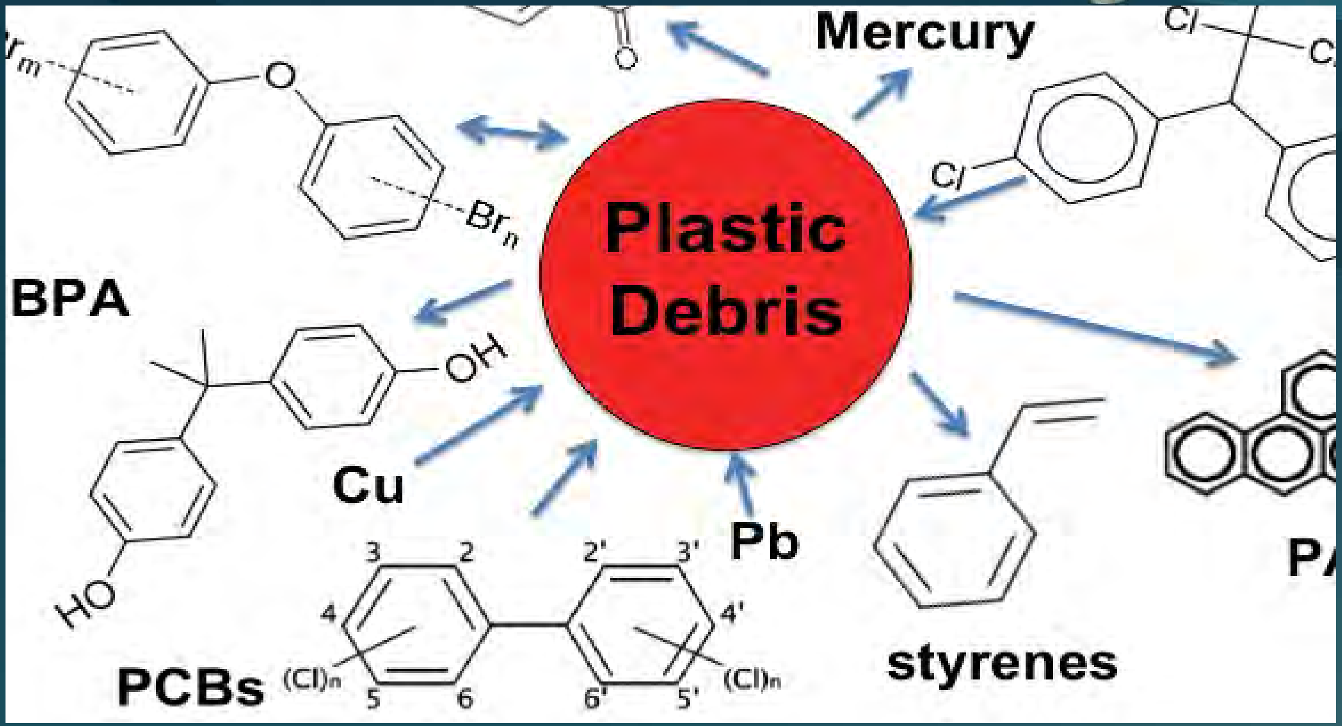
Food-Related Use

Polycarbonate plastic containers
Polymeric, epoxy resins in food and beverage cans
Clear plastic food wrap
Plastic tubing, storage containers used in industrial food production
Multiple uses in food manufacturing equipment Grease-proof paper and paperboard food packaging

Linked to: Diabetes, Obesity, Cancers, Behavior Disorders

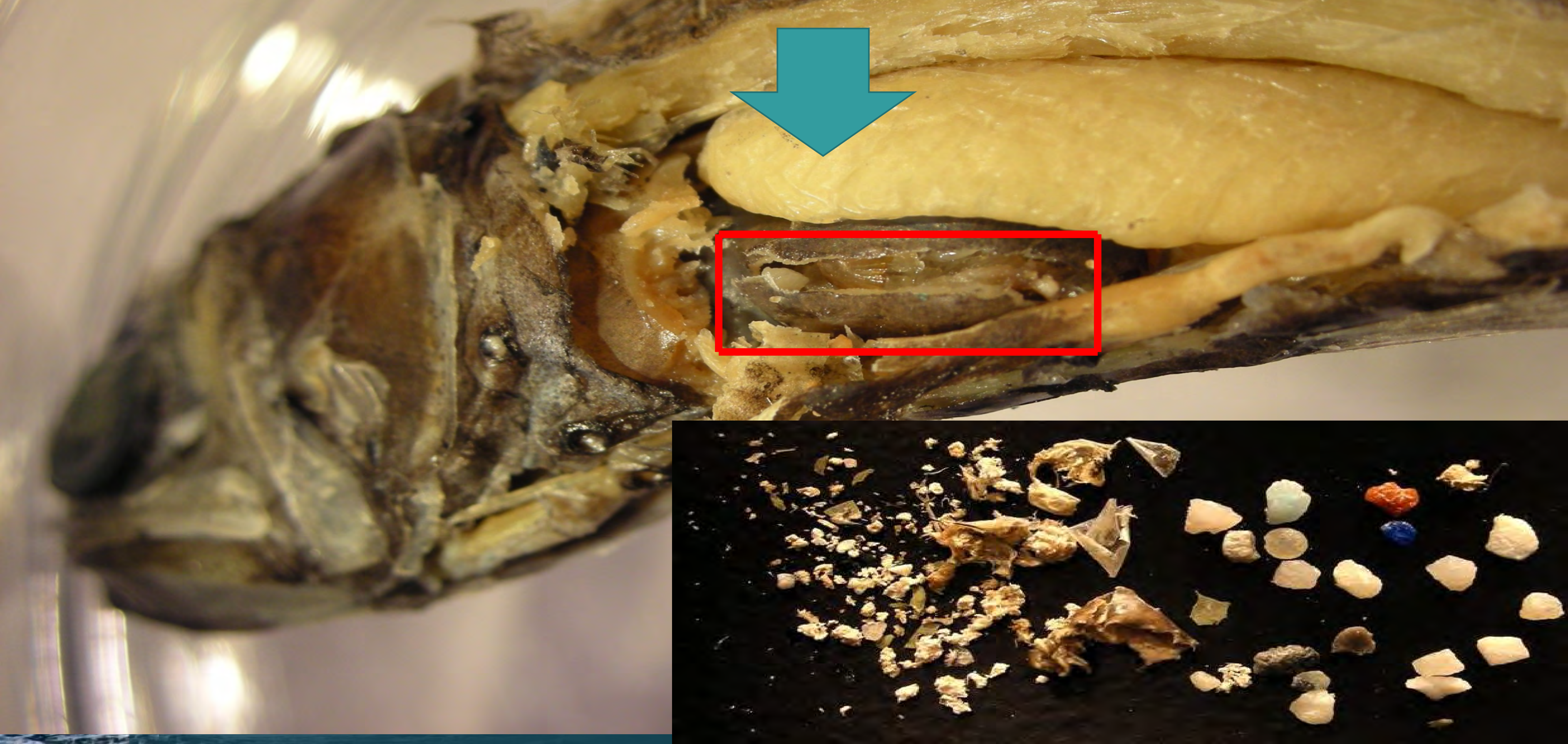
Food Additives and Child Health - Leonardo Trasande, MD, MPP, FAAP,a Rachel M. Shaffer, MPH,b Sheela Sathyanarayana, MD, MPH,b,c COUNCIL ON ENVIRONMENTAL HEALTH

Once in the ocean, like a sponge, adsorb and release chemicals



Plastic photo-degrades - breaks *up* into smaller and smaller pieces

Stomach Analysis – 670 planktivorous fishes 35% ingested plastics at an average of 2.5 pieces per fish (Boerger et al. 2010)



Can you tell which is the hydrozoan and which is the plastic cheese wrap?

Which is a piece of plastic bag and which is the pteropod?

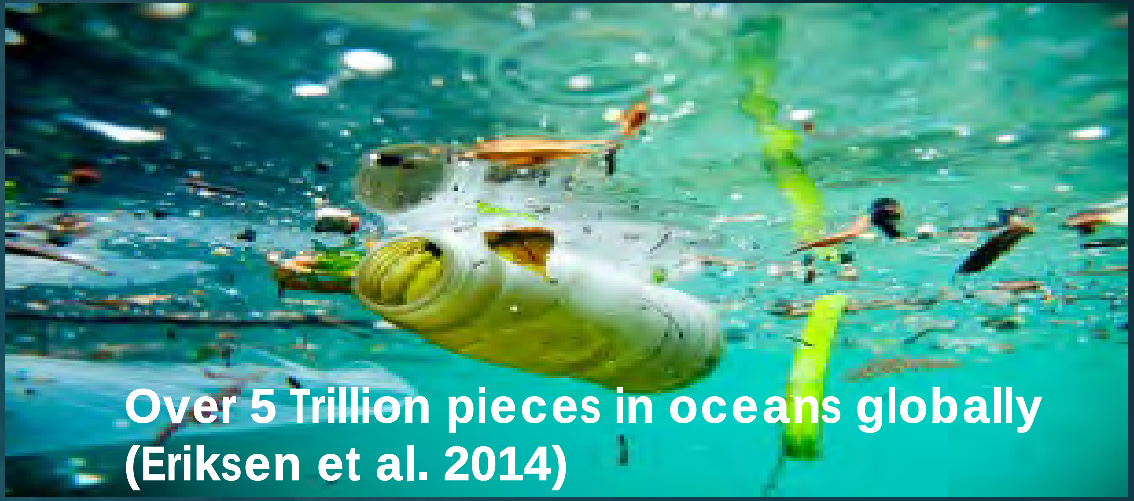

Not just small plastic pieces

Entanglement

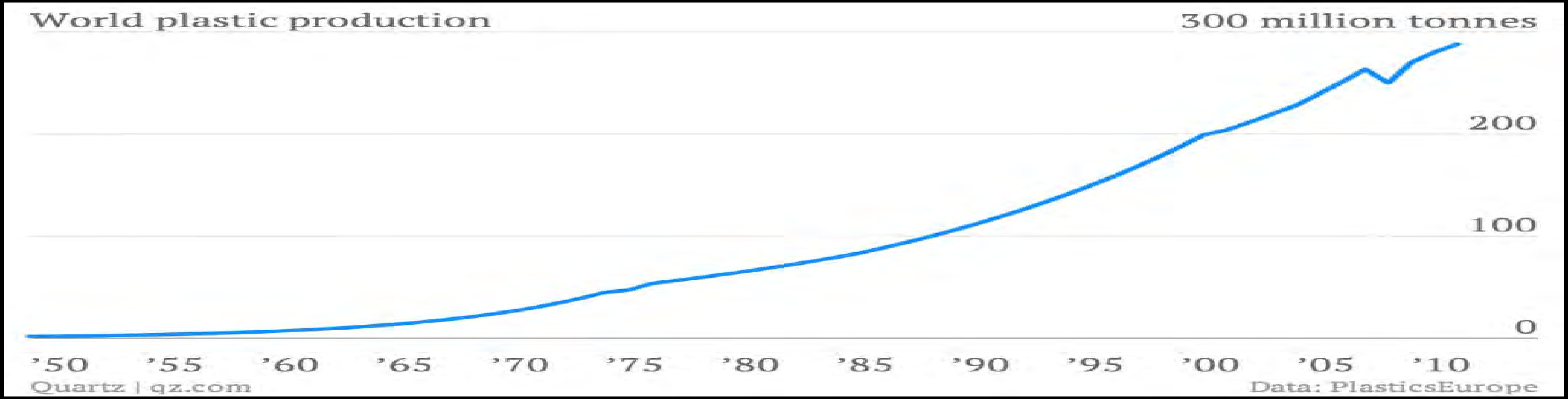
The results of one strand of fishing line

Plastic Ocean Project, Inc.

Ecological Concern on a Global Scale



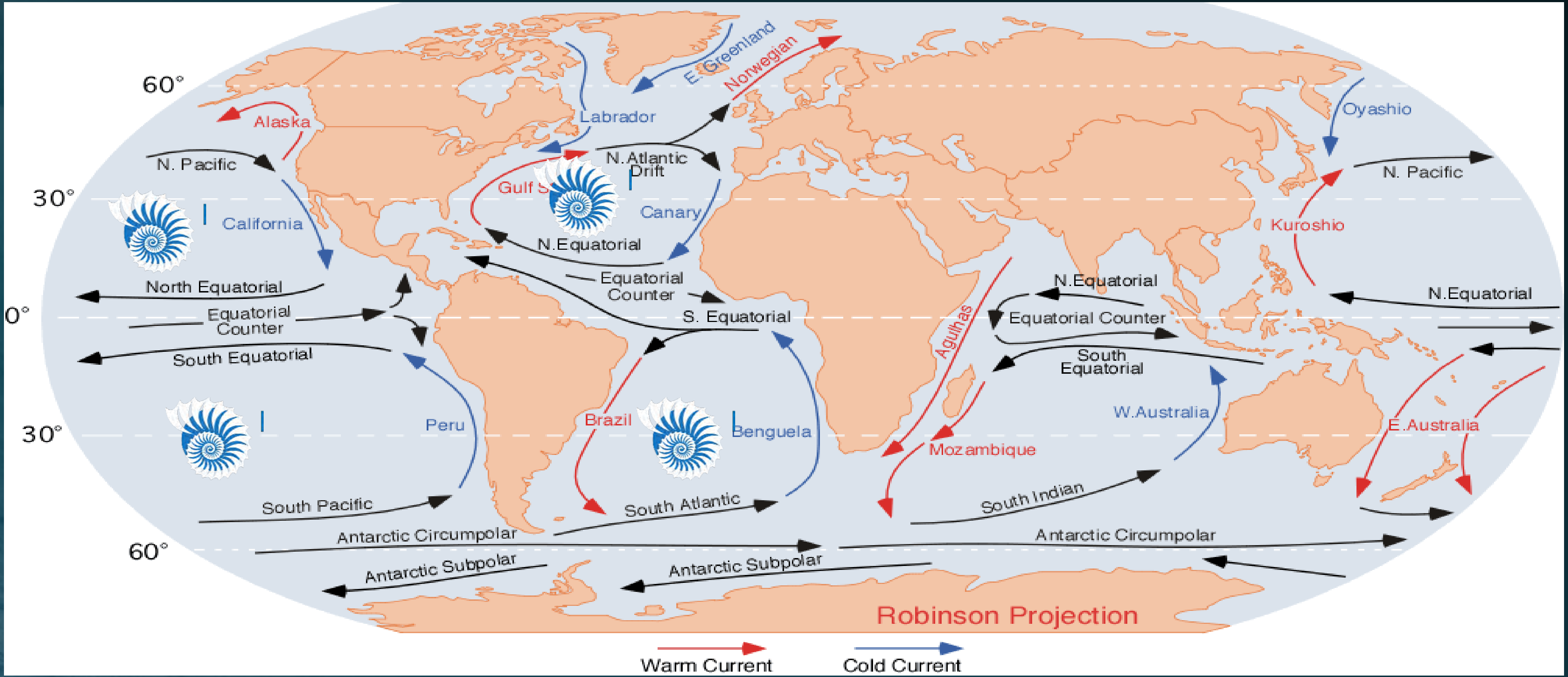
Plastics Global Consumption



- Ellen MacArthur Foundation states more plastic than fish 2050
- $180 billion to increase production by 40% within the next 10 year
- To date, only about 10-12% of plastics are recycled
- Outside of the small percentage incinerated (or launched into space), every piece of plastic ever made is still here

Over 10,000 nm sampling plastic marine debris

PLASTIC OCEAN PROJECT



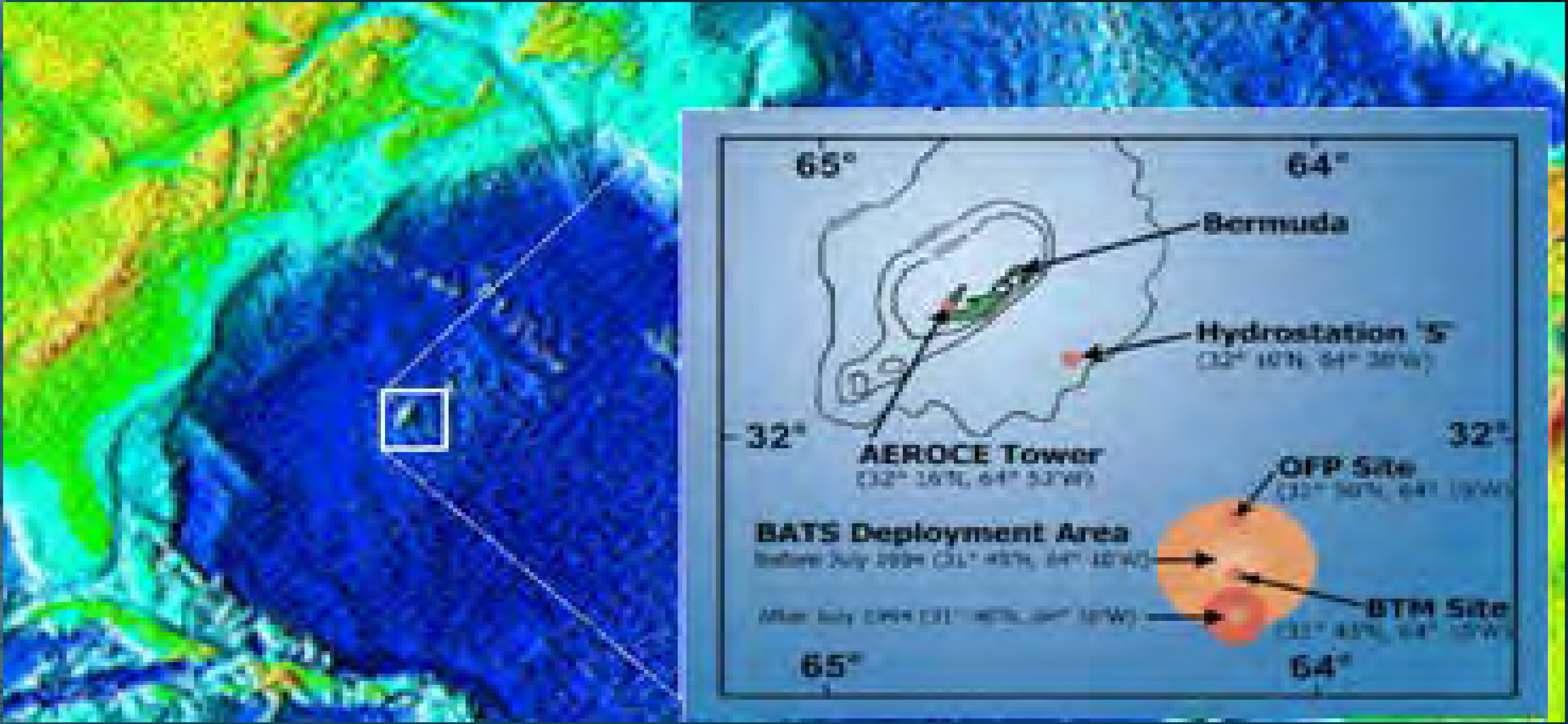
Education thru Research, Outreach thru Art, and Solutions thru Collaboration

Our Bermuda research since July 2009

Surface sampler

PIs Bonnie Monteleone and Jennifer O'Keefe

North Atlantic Sample site



PROCESSING THE SAMPLES

Typical surface sample predominately micro plastics Defined as 50 μm - 5 mm (0.05-5mm)

Results from first set of samples in the North Atlantic Sargasso Sea

Comparison between Carpenter and Smith (*Science*, **1972**, *175*, 1240-4), **11**-neuston net tows, 27 Sep – 18 Oct, 1971 and our **6**-manta (neuston) net trawls, 22-26 Jul 2009:

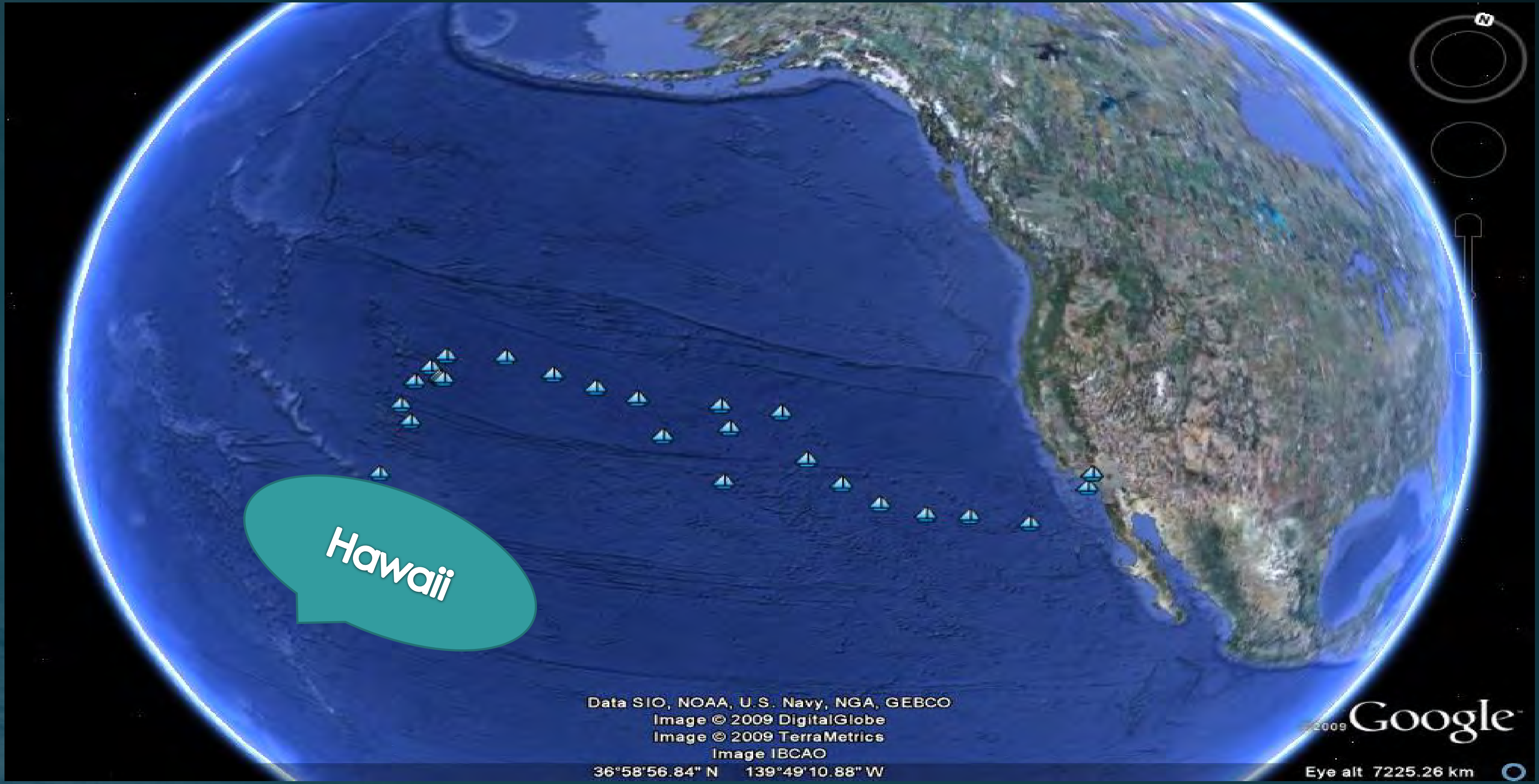
Sample	Carpenter and Smith (1972)	Monteleone et al. (2009)
	Plastic Particles (g/km^2)	
Low	0.6	23.8
High	1,771	3,570
Mean	287	977

Separated samples by size, type, and color
(1-2.36 mm, most fragments are white)

Rough Estimate from study
Sargasso Sea is 3,520,000 km= 3,440 tonnes of plastic fragments

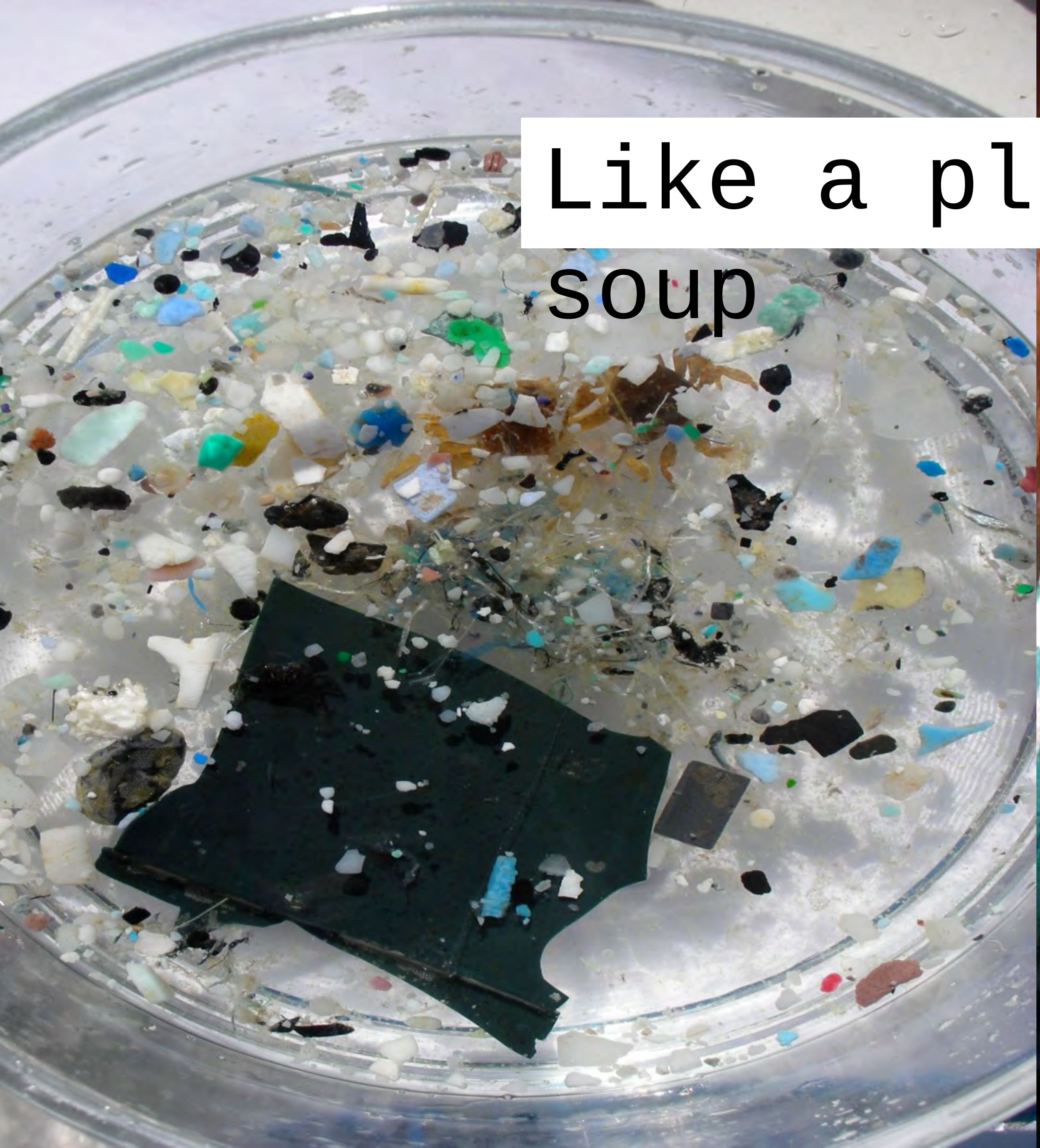
North Pacific Garbage Patch

Algalita Marine Research Foundation 10 Year re-sampling



Moore CJ1, Moore SL, Leecaster MK, Weisberg SB.
A comparison of plastic and plankton in the north Pacific central gyre. Mar Pollut Bull. 2001 Dec;42(12):1297-300.

Like a plastic soup



South Atlantic

4,600 nm from Rio de Janeiro to Cape town S. Africa sampling for plastic –Fall 2010

1 of 7 voyages around the world collecting samples for a global study working with citizens and scientists.

5 Gyres Institute

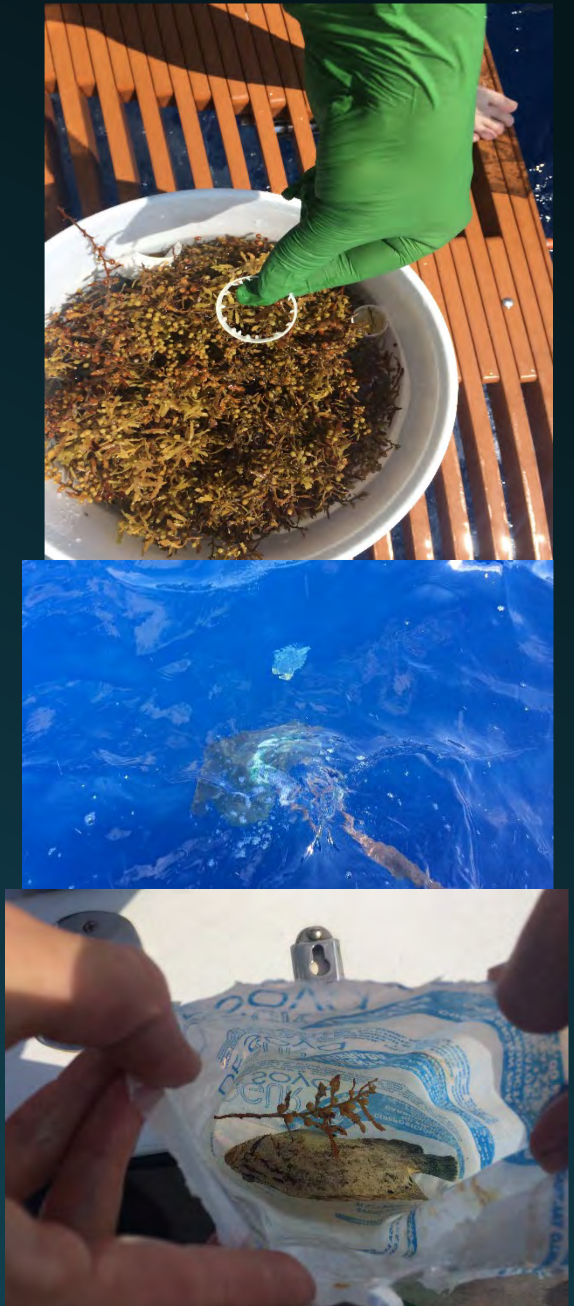
Eriksen et al. “Plastic Pollution in the World's Oceans: More than 5 Trillion Plastic Pieces Weighing over 250,000 Tons Afloat at Sea” 2014

South Pacific – filming of “A Plastic Ocean” – find it on Netflix

Developed and teach Marine Debris Field Research Course

- Hire charter fisherman
- Look for high pressure systems
- Temperature changes
- Currents

When we find *Sargassum, we find plastic*



Beach sampling

- Surveying beaches using scientific method
- Quantifying debris for data analysis
- Promote policy and legislation

Fishing4Plastic: Research Regarding Single-Use Offshore and Onshore Plastics

Summer Brooks
Meredith Smith
Michael Mosure

Research Goal

The ultimate research goal was to find the percentage of single-use plastics collected along the Gulf Stream during various offshore trips and the percentage of single-use plastics collected at onshore beach sweeps. The goal was to sort, quantify, and make observations of the type of plastics being recovered from the offshore trips, denoted on the map below, and onshore beach sweeps that took place at Wrightsville Beach and Kure Beach, North Carolina.

Introduction

What is the Fishing4Plastic Tournament?

- **The Fishing4Plastic tournament is a competition put on by The Plastic Ocean Project in which charter boats compete to collect the most plastic off the Gulf Stream.**

Why is it important?

- **Plastic is known to be harmful to organisms and to human health, it has potential to increase the transport of organic and inorganic contaminants, it presents a hazard to shipping, and it is aesthetically detrimental, thus generating negative socio-economic consequences (3).**
- **A 2014 study, from six years of research by the 5 Gyres Institute, estimated that 5.25 trillion plastic particles (weighing 269,000 tons) are floating in the sea (4).**

What are single-use plastics?

- **A single-use plastic is defined as "plastic materials that are disposable and generally used only once before they are thrown away or recycled" (5).**
- **It is estimated that 50% of plastic is thrown away after a single-use (4).**

About this experiment:

- **This experiment consisted of sorting through 1,278 pieces of identifiable plastics, categorizing them into single-use versus reusable plastics, and calculating the percentage of single-use plastics found off and onshore. Samples included unidentifiable plastics such as hard, film, and foam plastics (polystyrene). These plastics were also sorted and counted but not included in the percentage of identifiable single-use plastics.**

Our Hypothesis:

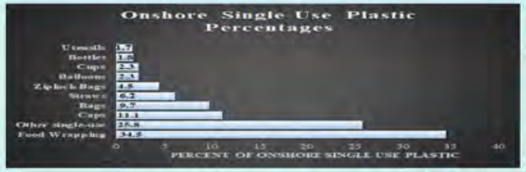
- **If onshore and offshore plastic is collected and sorted then 50% of the sorted plastic will be identifiable as single-use plastic.**

Methods and Materials

Methods:

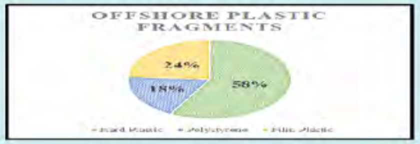
- Offshore samples were collected from:
  - June 2017 and October 2017 Fishing4Plastic tournaments
  - The Plastic Ocean Project team
  - Duke research teams
  - UNCW research teams
  - NC State research teams
- Onshore samples were collected from:
  - Fishing4Plastic beach sweep at Wrightsville Beach
  - UNCW POP Earth Day beach sweep at Kure Beach
- Samples were categorized by their date, coordinates, and surveyor(s).
- Samples were distributed across a flat surface and sorted using forceps, gloves, sifters, and the NOAA Marine Debris Shoreline Survey Field Guide. After each sample was laid flat, pictures were taken.
- To find the percentage of single-use plastic collected, the amount of on and offshore single-use plastic was divided by the total amount of identifiable plastic.
- Percentages were calculated for the top ten most common single-use on and offshore plastics collected.
- The GPS map was made using arcmap in esri arcGIS. All coordinates were converted to decimal degrees in excel.

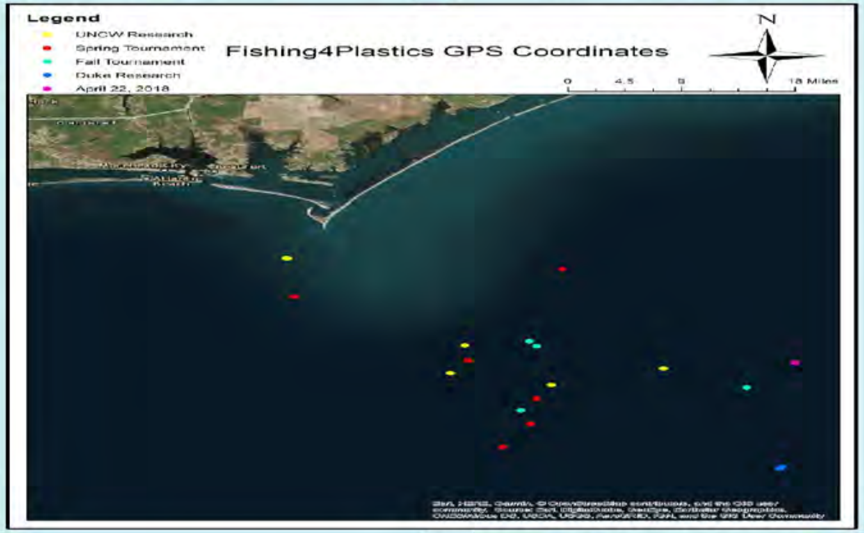
Results



These pictures show various samples that we sorted through. A piece of gum is shown to the right.

Summer Brooks collecting samples offshore on April 22, 2018





Conclusions

- From the offshore plastic sorted, 554 out of the 626 pieces of identifiable plastic were single-use resulting in a percentage of 88.5%.
- From the onshore plastic sorted, 597 out of the 652 pieces of identifiable plastic were categorized as single-use, resulting in a percentage of 91.9%.
- The most common single-use plastics found were food wrapping, caps, balloons, bags, cups, beverage bottles, ziplock bags, utensils, and straws.
- Food wrapping was the largest contributor of single-use plastic found on and offshore.
- Food wrapping made up 20.8% of the offshore single-use plastic collected and 34.5% of the onshore single-use plastic collected.
- The percentage of straws included in the single-use plastic percentage was expected to be higher in the offshore results; However, straws made up a higher percentage, 6.2%, of the onshore single-use plastic.
- Collecting samples from the segasm was incredibly difficult due to inadequate tooling. An improvement in the method could aid in the collection process.
- For future research, an increase in participation to collect and quantify larger amounts of plastic from all five gyres would provide a more accurate percentage and could be compared geographically to make more meaningful conclusions on single-use plastics.

Discussion

- What were the alterations to methodology?
  - The NOAA data sheets should be updated in order to more specifically categorize marine debris and include sections such as single-use plastics, ziplock bags, unidentifiable hard plastics, and unidentifiable plastic film.
- Relevant Policy (1):
  - Act to Prevent Pollution from Ships (APPS)
  - Marine Debris Research, Prevention, and Reduction Act (MDRPRA)
  - Shore Protection Act
  - Endangered Species Act
  - Marine Protection, Research, and Sanctuaries Act (MPRSA)
- Plastic bag bans have been successful in areas like San Francisco, Hawaii, and Washington D.C. and should be used as a stepping stone to more plastic bans such as, banning single use plastics. Imposing a fee on single use plastics, establishing a national deposit/refund system, and implementing producer responsibility programs are all potential policy recommendations (2).
- Challenges?
  - Quantifying the individual plastic pieces was a very tedious process that required delicate sorting in order to prevent small microplastic pieces from easily breaking into additional fragments. Transportation of the plastics to the counting labs may have also broken fragile plastics into additional pieces. These factors could potentially skew the results and must be considered.
- Microplastics:
  - Microplastics pertained, mainly, to the offshore plastics. A large amount of microplastics were found in the offshore samples. This shows that it's important that we collect the larger pieces of plastic before they break apart to create microplastics.

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GPS offshore map created in ESRI ArcGIS by Michael Mosure. Arisa Yoon for the offshore trip photo.
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Acknowledgements

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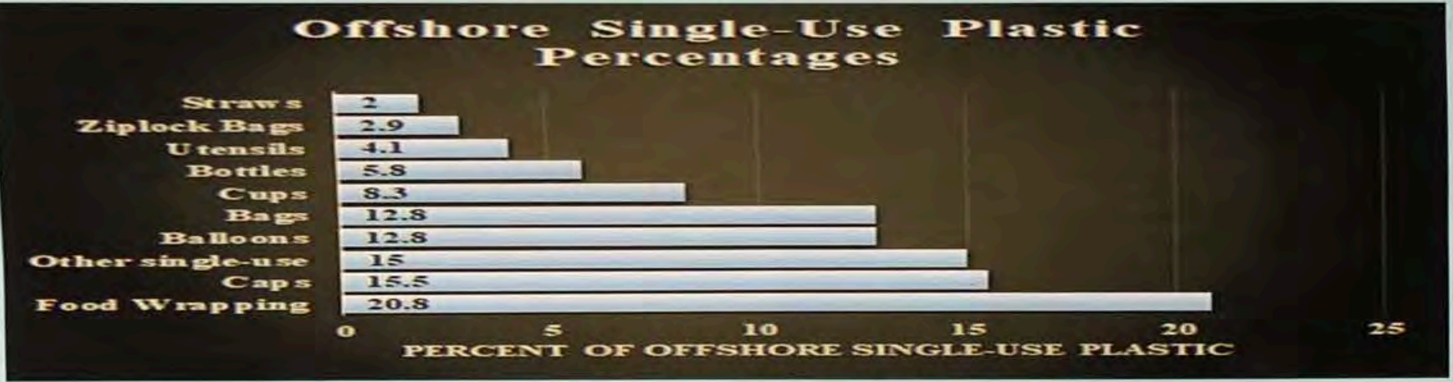

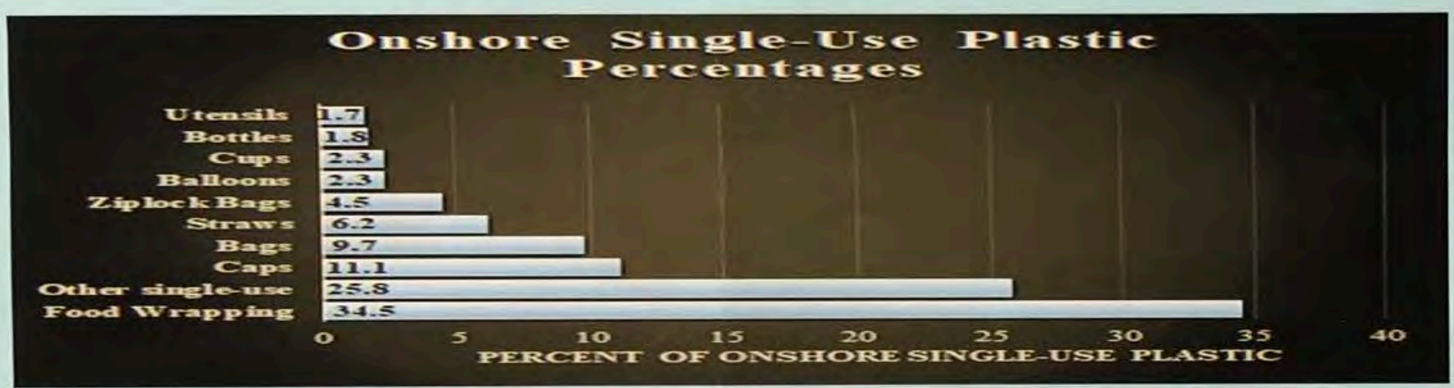

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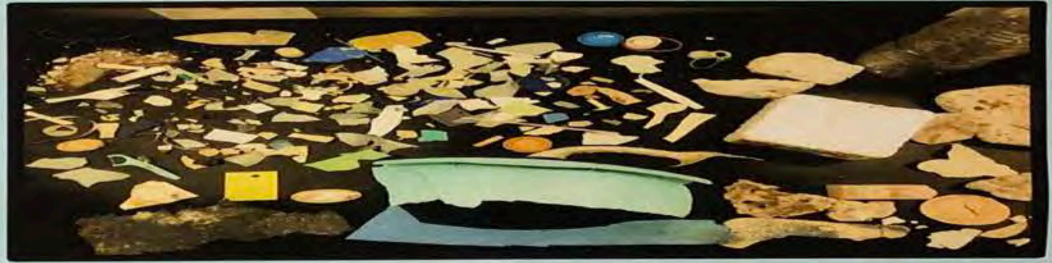

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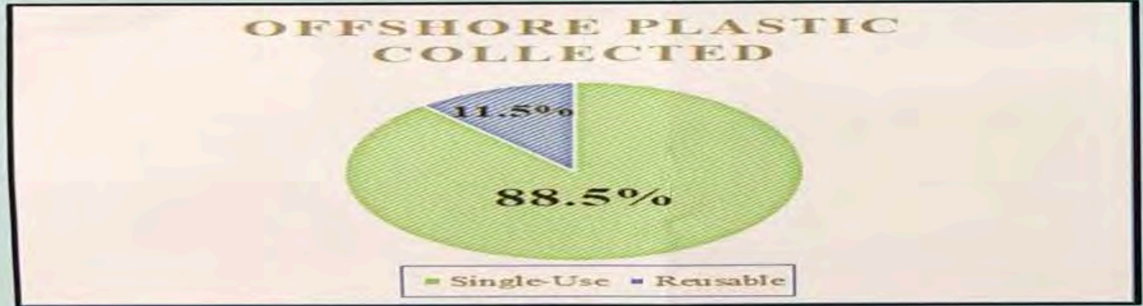

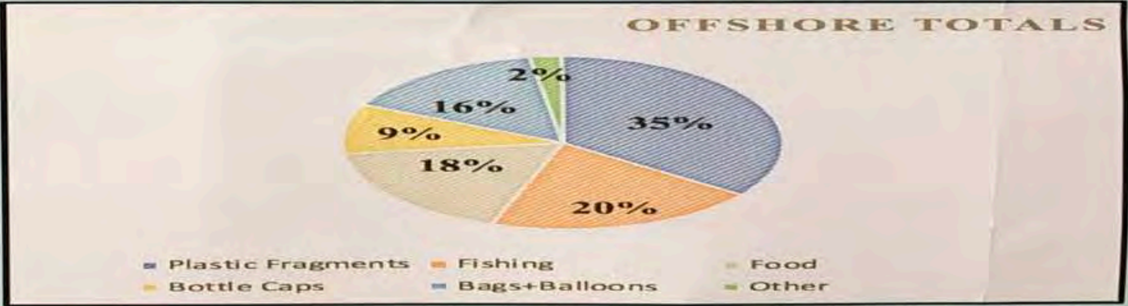

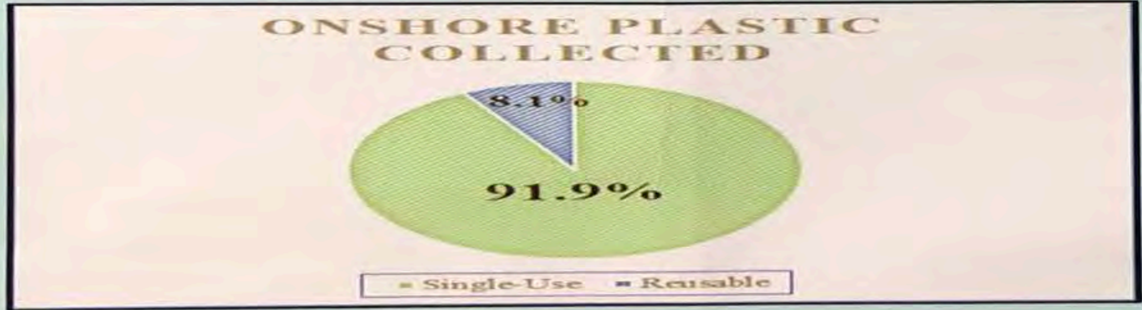

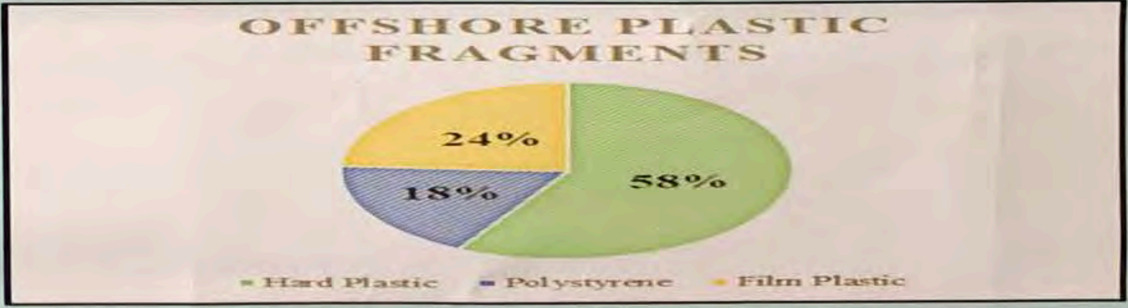

Assessing Marine Debris through Stormwater Regulation in Wilmington, NC

Allison M. Lapinsky, Addie K. Young, and Megan E. Lapinsky
Department of Environmental Sciences
University of North Carolina Wilmington

INTRODUCTION

Anthropogenic litter is commonly found polluting many natural environments in today's world. Whether it be on land or in aquatic environments, litter is unsightly and is harmful to many forms of life, as represented by the 8 problems listed below. When litter is managed improperly, it is carried into waterways during storm events and is eventually deposited into our oceans, where it becomes marine debris ("Sources of Aquatic Trash", 2017). Plastic litter represents a large portion of this marine debris. Trash originating on land makes up about 80% of marine debris and the other 20% stems from at sea disposals ("Toxicological Threats of Plastic", 2017). Large cities and towns produce high amounts of litter, and with an increasing global population, this poses a potential problem for our waterways. While litter travels downstream it disrupts natural processes and threatens human and environmental health ("Assessing Litter Loading", 2017).

This study was based off a pilot project performed by the Duke Environmental Law and Policy Clinic. In this study, four waterways in Wilmington, North Carolina were surveyed. Two of them drain into the Intracoastal Waterway (Bradley Creek and Hewletts Creek) and two drain into the Cape Fear River (Greenfield Lake and Burnt Mill Creek). It is hypothesized that if a stormwater pollution problem is present in Wilmington, North Carolina, then the waterways will have a high impairment score. The predetermined impairment scores were used in the Duke Environmental Law & Policy Clinic pilot project.

8 Problems with Plastic Pollution

- Loss of beach front value
- Plague marine nurseries
- Transport invasive species
- Entangle and capture marine life
- Navigational hazard for marine life and people
- Absorb and leach chemicals
- Ingested by marine life
- Interfere with the benthos

(Monteleone, 2011)

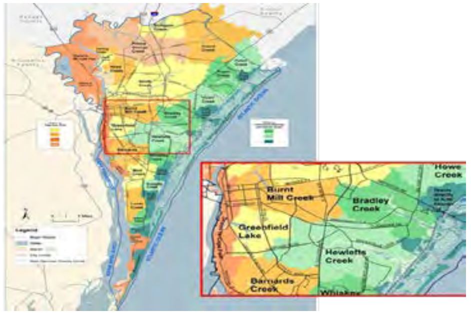

Figure 1. Watersheds of Wilmington.

PHOTOS

Dead crawfish in metal can.

Trash hotspot at Bradley Creek.

METHODS

Sampling Process: Prepared by the Duke Environmental Law & Policy Clinic

1) Travel to selected sampling site with equipment
2) Measure and mark three 30 meter transects with two 30 meter buffers in-between
3) Collect anthropogenic litter present from the center, sides, and one meter up each bank within the transects, keeping each transects' litter separated
   - Exclude buffer transects
4) Sort collected litter by transect according to specific categories (plastic film, hard plastic, styrofoam and other foams, metal, glass, and other material)
5) Record all data: state the type of litter while the note-taker records the number of litter items and identifiable brands on the data sheet
6) Dispose of trash properly

RESULTS

Figure 2. Overview of types of litter and common brands.

Sample Site	Average Number of Litter Items per 30 meter Transect	Impairment Score
Bradley Creek	451.3 ± 243.3	High
Burnt Mill Creek	242.3 ± 72.5	High
Greenfield Lake	429.7 ± 155.2	High
Hewletts Creek	261.0 ± 64.7	High

Figure 3. Average amount of litter per site with standard error and impairment score.

Figure 4. Total number of litter items collected at each site.

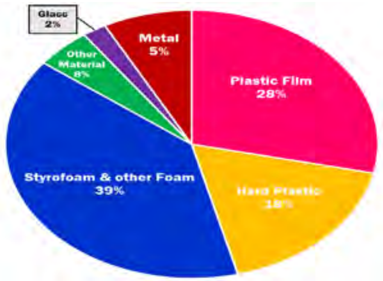

Figure 5. Percent total of each litter type found.

CONCLUSIONS

There is a stormwater pollution problem in Wilmington, North Carolina. High impairment scores were calculated in all surveyed waterways. About 90% of all litter collected was plastic materials. Single use plastics were frequently observed at all sites. After completing this research, we feel that the data collection sheets could be improved to better represent the litter load. Transects were modified at Burnt Mill Creek due to environmental hazards. The information obtained from this research could be used to support stormwater legislation in North Carolina. We hope to shed light on plastic pollution and continue research from which policy can be implemented to preserve our natural environments.

References and Acknowledgments

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We would like to thank Talia Sechley, Bonnie Monteleone, Edward (Ned) Buddy, and Dr. Michael Mallin.

Chemical Recycling

Researching a solution with Renewlogy (formally PK Clean)

- 2 + 2 Program students
- Local business involvement
- Organic chemistry
- Circular economy technology

Mindy Rodriguez, Dr. Seaton,* Dr. Mead, and Bonnie Monteleone
Chemistry Department
University of North Carolina Wilmington
mnr9774@uncw.edu

Volatile Organic Compounds From Plastics

Abstract & Introduction

World plastic consumption has increased dramatically over the past 60 years yet little research has been done on the chemical compounds escaping plastics. Volatile organic compounds (VOCs) are leaching out from plastics at both elevating temperatures and at room temperature. This research compares VOCs leaching from different plastics and at elevating temperatures.

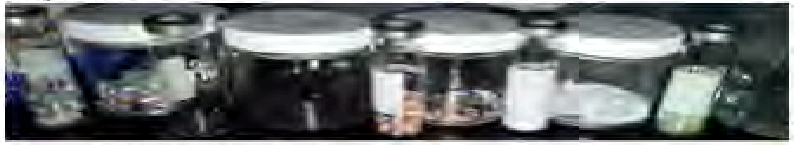

Figure 1: Plastics that underwent GCMS.

Methods

The plastic samples were obtained from black monochromatic plastic, general household plastic wrappers, plastic utensils, plastic lids from bottles, plastic used for shipping, and known preproduction plastics purchased from Sigma Aldrich which are found in plastics. Some plastics were placed in a grinder along with dry ice to ensure VOCs would not escape when grinded. After they were grinded, they were placed in sealed containers. Headspace vials were filled to ¼ full with the plastic samples. The vial was capped and sealed. The Headspace GC/MS Bruker SHS-40 was used to analyze. Plastics in vials were heated at 80°C for ten minutes in the headspace unit. 1 µL of the gas was then injected into the GC/MS. The GC temperature programs started at 30°C for five minutes and increased at a rate of 20°C per minute to 200°C. Mass spectra of peaks from each chromatogram were compared to the NIST MS-library and to MS from peaks from standard plastics and identified where possible.

Figure 2: Headspace GC/MS Bruker SHS-40 that was used for analyzing the VOCs.

Discussion

When analyzing the VOCs from the plastics, there were similar peaks that arose. The most common chemical compounds that were found were styrene, propyl benzene, and ethyl benzene. Styrene and ethyl benzene are used for fuel additives, paint and coating additives, rubbers, and plastics. Propyl benzene can be used in fuel additives as well. These VOCs have short-term and long-term effects on humans and animals. Short-term human exposure to styrene, propyl benzene, and ethylbenzene can experience mucous membrane irritation and eye irritation. Propyl benzene is mildly toxic if ingested or inhaled.[1] All of these compounds have not been found to be carcinogenic to humans, but propyl benzene has been found to be carcinogenic to animals.[1] A study done on female workers in plastic industry reported increased spontaneous abortions and a decrease in births.[2] It is not known if the plastics had an effect on reproductive or development of fetus. The plastic fork and knife combination contained all three VOCs and leached the most VOCs out of all the plastics analyzed. The general plastic, plastic lids, and the fork and knife plastic utensil had similar peaks of styrene and ethylbenzene leaching out in similar times.

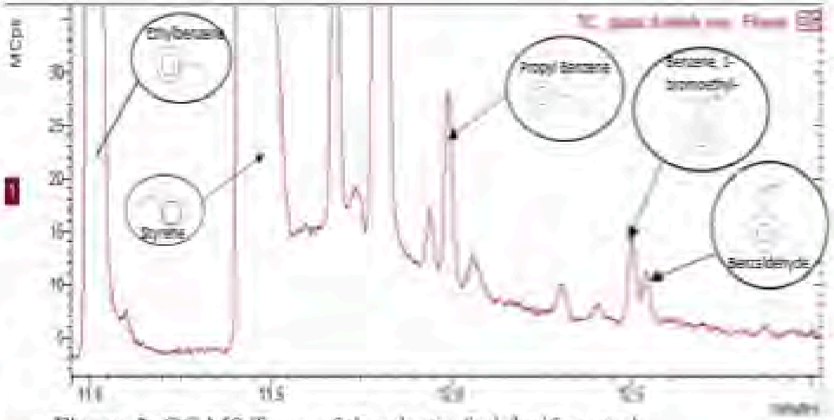

Figure 3: GC MS Trace of the plastic fork/knife sample.

Conclusion

Out of all the plastics analyzed, the plastic lids and the plastic bags leach the least. The mixture of forks and knifes leach the most out of all the plastics. The most common volatile organic compounds that leached were styrene, propyl benzene, ethyl benzene. These compounds may not be carcinogenic to humans, but can have negative health affects on human respiratory and central nervous systems. Benzaldehyde was found in the plastic fork/knife sample. Benzaldehyde has physical properties that makes it hazardous to the environment. Benzaldehyde can contaminate groundwater since it sinks in water.[3] Further analysis of plastics should be done to grasp a better understanding of the human and environmental impact from plastic consumption.

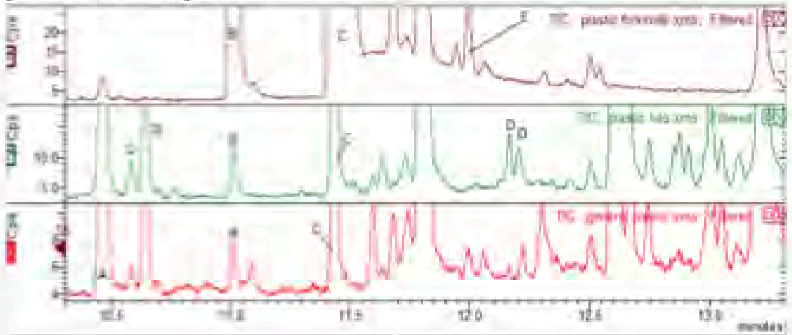

Figure 4: GC MS Trace from some of the plastic samples. The letters denote different chemical structures found (A= alkane, B= ethylbenzene, C= styrene, D= branched alkane, E=propyl benzene).

References and Acknowledgements

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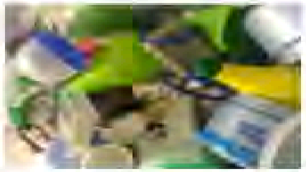
UNCW Student Fee-Based Green Initiative Fund

Plastics to oil, NMR and GC/MS characterization of oils produced from a variety of plastics under a variety of reactor conditions.

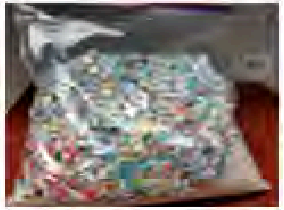
Pam Seaton, Matt Anttila, Judson Bledsoe, Bonnie Monteleone, Ralph Mead
Department of Chemistry and Biochemistry, University of North Carolina Wilmington

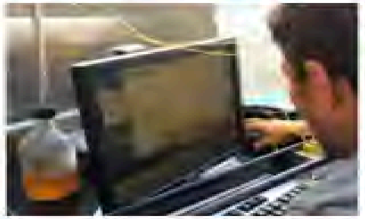


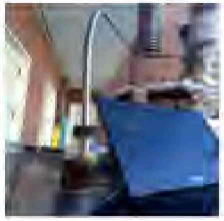
Background

Plastics waste ranks among the highest municipal and industrial waste. Solutions for plastics waste has been limited to: landfilling that accelerate the need for landfill space, incineration that emit known carcinogens such as dioxins, and recycling which eventually enters the waste stream. Plastic trash that do not reach municipalities can enter aquatic regions causing overall financial damage estimated at roughly $14 billion annually from harm inflicted on marine ecosystems. (UN Environmental Assembly)

Converting plastics to oil is emerging as a new waste management technology. This study analyzes oil rendered through a pyrolysis process using a prototype reactor at UNCW. The characteristics of the resulting oil depend on the plastics used and the reactor and distillation conditions. We varied reactor and reflux temperatures for a variety of plastics, including pure polyethylene and polypropylene, as well as mixed plastics from beach clean-up samples and plastics collected from the Sargasso Sea. Oils were characterized by 1D and 2D NMR and GC/MS. Oils from primarily polyethylene (PE) were found to be composed of a series of straight chain alkanes and terminal alkenes while oils from polypropylene (PP) contained more branched alkanes, alkenes and aromatics.



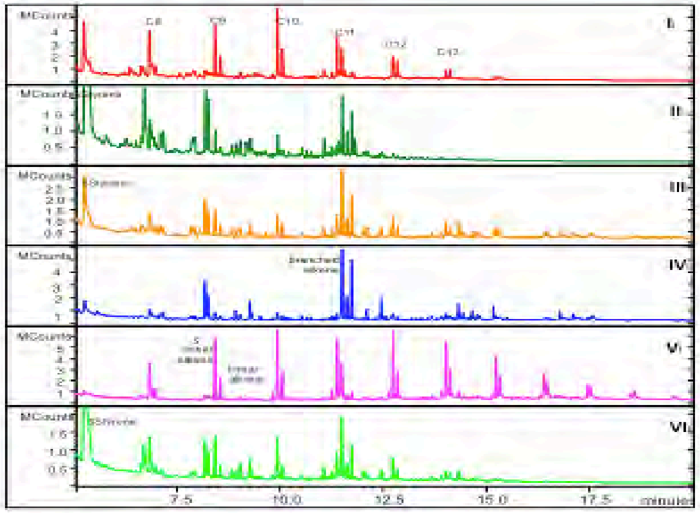




Material and Methods

- Collect and sort plastic by the American Section of the International Association for Testing Materials(ASTM) resin identification code. When using When using indistinguishable plastics, toxic polyvinyl chlorides were separated by density.
- Granulate plastics using IKA grinder
- Weigh and load in Depolymerizing Reactor.
- Fracture plastics at high temperatures and condense vapors into oil or wax, collect into graduated jar
- GC/MS samples prepared by diluting condensates (50 uL) in hexane (1 mL) and diluting again (10 uL in 1 mL).
- NMR samples prepare in CDCl3 (50 uL in 500 uL)

Results



I. Marine plastics:
II. Beach Plastics (Wrightsville)
III. Household waste
IV. Polypropylene Caps
V. HDPE Jugs
VI. Shipping Materials:

Figure 1. GC/MS of oils from 6 plastics, Varian Saturn 2200, DB5 column, temperature program 40C, 1 min., 40 – 320°C 10°C/min.

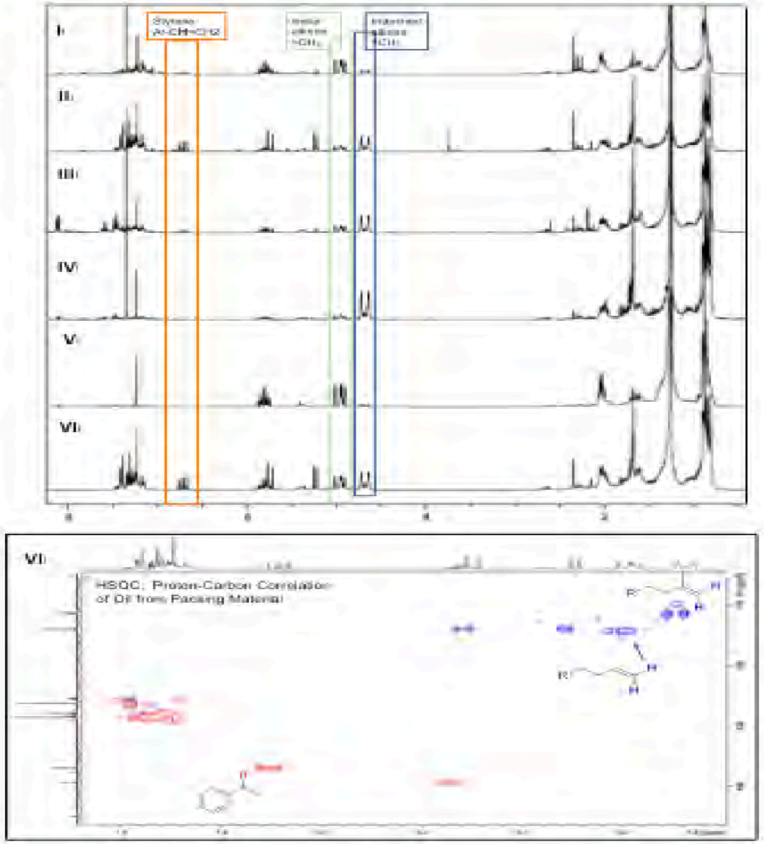


Figure 2. NMR, 300 MHz of oils from 6 plastics. *Top*, H-NMRs showing alkene signatures from styrene PE and PP; bottom, H-C correlation experiment used to confirm assignments

Findings and Future Work

- The type of plastics determine the chemical profile of the oils:
  - Polyethylenes produce primarily straight chain alkanes and terminal alkenes.
  - Polypropylenes produce branched alkanes an alkenes.
  - Polystyrenes produce complex mixtures containing a high percentage of styrene
  - Mixed plastics give complex mixtures of all of the above, usually containing a higher percentage of aromatics
- High return of oil to plastic, close to 1 to 1 (500 g produced 498 mL oil)
- Most oils appear to have relatively high cloud points.
- Paraffin seems to be a viable production.
- Changing the temperature in the of unit and reflux had little effect on sample composition
- **Future Work:**
  - Test cloud point, flash point, using ASTM standardized test D-975 and D-93. to verify fuel quality.
  - Capture volatiles, analyze and investigate for potential heating source for reactor.
  - Trap and analyze, using static head space GC, off gases of simply disposed plastics.

Acknowledgements

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Household Waste to Oils

Heather Wurtele, Pam Seaton, Bonnie Monteleone, Ralph Mead, and Judson Bledsoe
University of North Carolina Wilmington

Abstract and Method

Using a countertop batch reactor, two different oils were produced and fractionated from household waste feeds. These oils were characterized using GC-MS and NMR techniques. The oils, although in different proportions, contained: long chain alkanes and alkenes, styrene, and other aromatic compounds. Physical properties of these oils, including flash points and cloud points were also determined and found to be similar. The ultimate goal of this process is the production of new petroleum products while providing a new fuel source and recycling low value plastics.

Four Fractions were obtained from rotovapping at a medium vacuum and different temperatures (30°C, 40°C, 50°C, 70°C respectively). The remaining fraction was pulled from the RB flask. Safety concerns were mitigated using proper disposal of compounds, ventilation, and personal protection equipment including glasses, lab coat, gloves, etc.

Compound(Hydrogen)	Location (ppm)	Original	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction remaining
Aromatic	7.54-7.09	1.00	1.00	1.00	1.00	1.00	1.00
Alkene	6.85-4.60	0.96	0.9	0.77	0.8	0.80	1.52
Alkyl chain	1.5-0.4	8.77	6.77	5.53	5.29	6.03	25.02

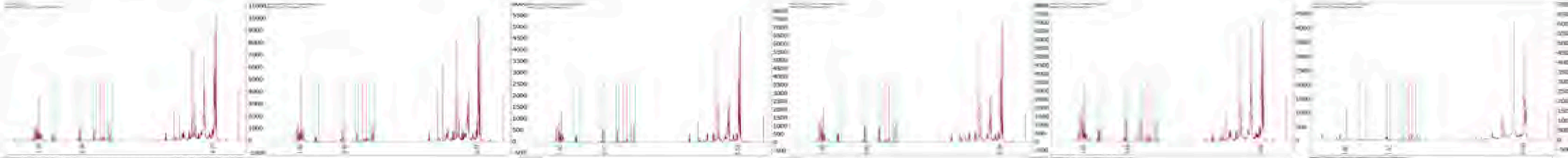
Figure 1. Integration information for Figure 2-7, HHW oil for 5/16/17

Compound(Hydrogen)	Location (ppm)	Original	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction remaining
Aromatic	7.54-7.09	1.00	1.00	1.00	1.00	1.00	1.00
Alkene	6.85-4.60	1.14	1.29	0.81	0.79	0.82	2.02
Alkyl chain	1.5-0.4	9.10	6.69	3.89	3.49	3.80	34.69

Figure 2. Integration information for Figure 9-14, HHW oil for 6/28/17

Findings and Future Work

- Batches of Household Waste materials are relatively the same in chemical makeup
  - Styrene
  - Branched/linear alkenes and alkanes
  - Other Aromatic compounds
- Investigate chemical and physical property relationships including
  - Increasing/decreasing temperature of reactor
  - Changing composition of feed into reactor
  - Pour point (temperature not reached)
  - Flashpoint (-16°C for original HHW 6/28/17)
  - Cloud point (<-12°C for original HHW 6/28/17)



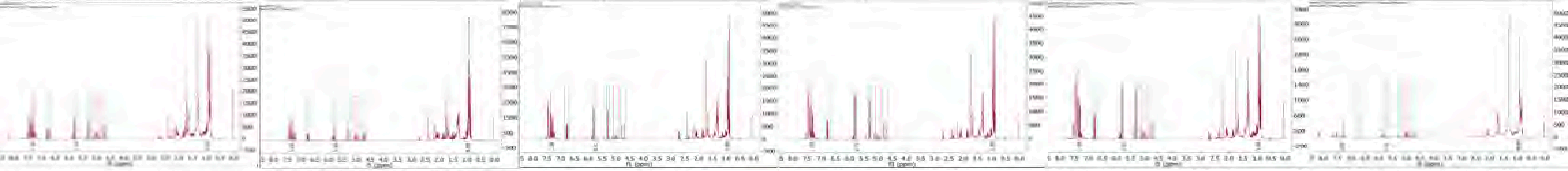
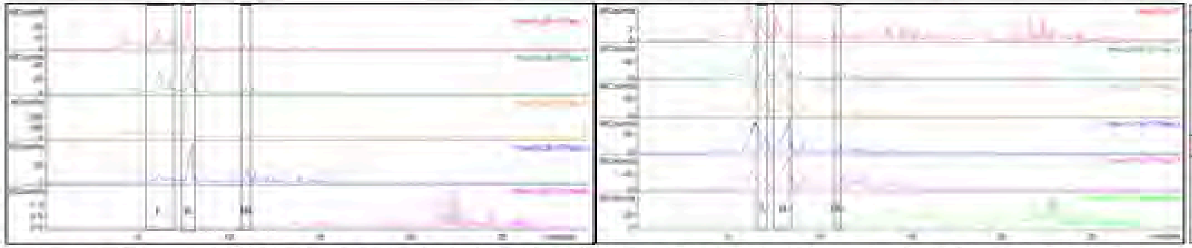


Figure 9. Original, 6/28/17 Figure 10. Fraction 1, 6/28/17 Figure 11. Fraction 2, 6/28/17 Figure 12. Fraction 3, 6/28/17 Figure 13. Fraction 4, 6/28/17 Figure 14. Remaining Fraction, 6/28/17



Figur 1 GC/MS of batches of HHW 6-28-17 (left) and 5-16-17 (right) oils ; Varian Saturn 2200, DB5 colum per ture program 40°C, 2 mins.;40-100°C:4°C/min, 2 mins.;100-280°C:10°C/min, 6 mins

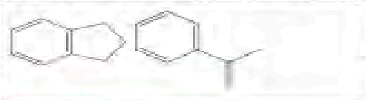
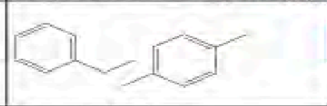
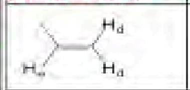
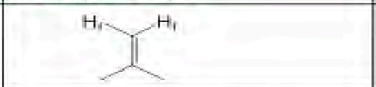
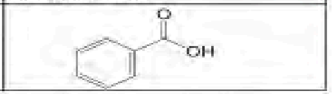
Styrene (II.)	Indane or α-methylstyrene (III.)	Ethyl benzene or xylene (I.)
		
Linear Alkene	Branched Alkene	Benzoic Acid
		

Figure 15. Common compounds found in the oils producing distinctive peaks (Color coded on NMR) (Roman numerals on GC-MS)

Acknowledgements

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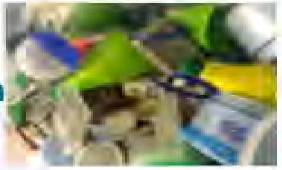


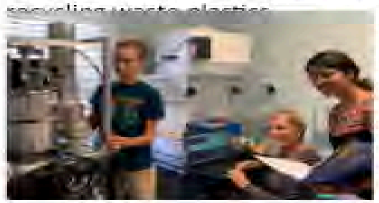
PLASTICS TO OIL

Pam Seaton, Heather Wurtele, Jincy Joseph, Callie Dalton, Ralph Mead, Bonnie Monteleone
Department of Chemistry and Biochemistry, University of North Carolina Wilmington, Plastic Ocean Project,

Abstract

Global plastic litter entering the oceans was estimated to be roughly 20 million metric tons in 2010. This staggering amount of plastic litter is transported by ocean and wind currents and results in large quantities of plastic particles floating throughout the oceans and depositing on beaches. Converting plastics to oil is emerging as a new waste management technology and could provide a means to convert growing amounts of plastic debris accumulating on islands into valuable products.

Oils produced from marine, household and pure plastics were pyrolized using a countertop pyrolysis reactor and characterized by NMR, FTIR and GCMS. The oils contain long chain alkanes and alkenes, styrene, and other aromatic compounds, in differing proportions, depending on the plastic feedstock. Polystyrene (PS) pyrolysis produces styrene as the major component along with many larger aromatic compounds, including polyaromatic hydrocarbons (PAH), which have been quantified using GCMS. PAH concentrations varied with plastic feedstock, however most were in the range of PAH concentration in diesel. Physical properties of the oils were found to be comparable to commercial fuels. The carbonyl index (C=O) was analyzed as a measure of thermal stability of the oils. Oils containing PS showed the greatest increase in C=O index. NMR analysis confirmed new carbonyl signals. Through these analyses, and by changing the composition of feedstock plastics, our goal is to use pyrolysis of waste plastics to produce a safe fuel alternative, while recycling waste plastic.



Materials and Methods

- Collect and sort plastic by the American Section of the International Association for Testing Materials(ASTM) resin identification code. When using
- Fracture plastics at high temperatures, collect condense oils in glass jar
- FT-IR: A Thermo scientific Nicolet iS5 spectrometer equipped with an iD7 attenuated total reflection (ATR) diamond crystal accessory was used to collect spectra from 4000 cm^{-1} to 500 cm^{-1}. Essential FTIR software was used to process the spectra to calculate the carbonyl index
- GC/MS: oils (50 uL) diluted in hexane (1 mL) and further diluted (10 uL in 1 mL) for full scan analysis. For PAHs, diluted fractions were analyzed using an MRM protocol.
- NMR: oils diluted in $CDCl_3$ for 1D and 2D NMR using 500 and 600 MHz Bruker
- Stability: Oils were heated at 60 ^{0}C in glass vials for 0, 1,2,3,4, and 8 weeks
- Physical properties: Flash points were measured on a SYD 261 closed cup flash point tester from Shanghai Changii Geological Instrument Co Ltd.
- Pyr[illegible] ja[illegible] om[illegible] Scientific) were used to conduct cloud and pour point tests

Results

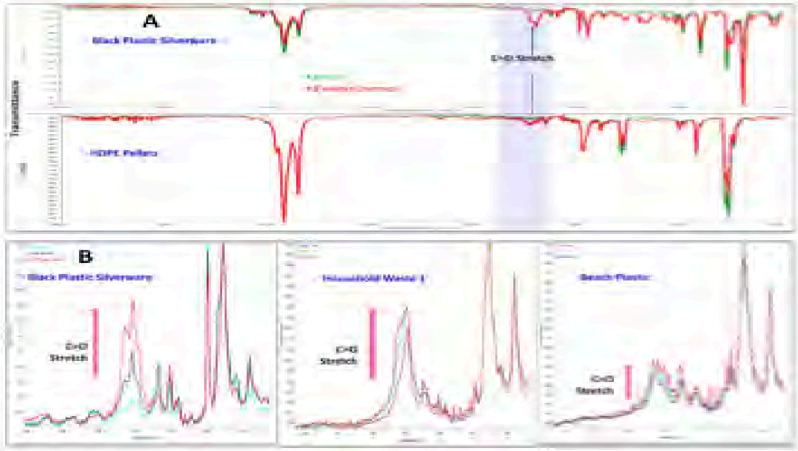


Figure 1. A. FTIR-ATR spectra (initial and 8 weeks thermal) of oil from black plastic silverware and HDPE pellets showing increased intensity in C=O stretching region.
B. Spectral expansions of carbonyl region

B	HDPE Pellets	PP Pellets	Plastic Bags	HHW2 Household Waste I	Hawaii	Oil 203	Black Plastic Silverware	HHW1 Household Waste I	Atlantic Beach	Diesel
% Styrene	0	0	0	1	4	90	85	26	34	0
% Linear	100	0	100	25	63	0	15	31	17	0
% Branched	0	100	0	74	33	10	0	43	48	0
Σ PAH (ug/g oil)	-	-	27	21	-	-	78	17	74	22
% Recovery	80% *	80% *	37% **	57% **	67 % *	83% *	61% **	70% **	50% **	
Density (g/mL)	0.78	0.77	0.75	0.78	0.79	0.89	0.87	0.77	0.83	
Cloud Point	-9 °C	-4 °C	5 °C	10 °C	15 °C	1 °C	0 °C	3 °C	0 °C	-15 °C
Flash Point	-6 °C	12 °C	-67 °C	77 °C	10 °C	16 °C	13 °C	13 °C	58 °C	58 °C

*Non-small Pyrolysis chamber **Large Batch Pyrolysis chamber

Figure 2. A. Carbonyl Index Values from thermal treatment of oils (red = 8 weeks, green = 4 weeks, blue = 2 weeks, orange = initial C=O Index value). B. Alkene distribution by NMR integration, ΣPAH from GCMS MRM and physical data for the various oils.

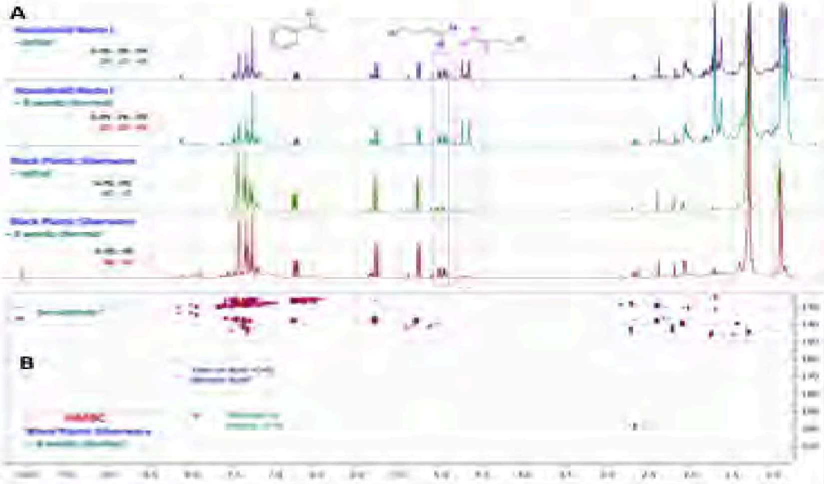


Figure 3. A. ^{1}H-NMR of Household Waste 1 and Black Plastic Silverware Oils, before and after 8 week thermal treatment. B. HMBC (600 MHz NMR) of aromatic and carbonyl region showing new correlations to carbonyl carbons in the thermally treated Black Plastic Silverware Oil.

Findings and Future Work

- The type of plastics determine the chemical profile of the oils:
  - Polyethylenes produce primarily straight chain alkanes and terminal alkenes.
  - Polypropylenes produce branched alkanes an alkenes.
  - Polystyrenes produce complex mixtures containing a high percentage of styrene and aromatics
  - Mixed plastics give complex mixtures of all of the above, usually containing a higher percentage of aromatics
- Oils with high styrene content show increased carbonyl index values. NMR shows that styrene is preferentially lost from thermally treated oils. 2D NMR shows that new carbonyl containing compounds are produced in the thermally treated oils.
- Oil from beach plastic contains highest total PAH.
- Cloud points of the oils are relatively high compared to commercial fuels while flash points are more variable.

Future Work:

- Using new continuous feed pyrolysis reactor, produce oils from pure plastic pellets for comparison with oils from single plastic waste plastics and mixtures.
- Vary plastic mixtures and pyrolysis temperatures to produce an oil with desired characteristics.

Acknowledgements

Renewology
Plastic Ocean Project, Inc.
Making a Mark Family Foundation
Current Electric,
IKA Laboratory Equipment

Solving the Plastic Rubik's cube problem

Blue New Deal

made possible with **bipartisan leadership**

Our oceans sustain our economy, generate 50% of our oxygen, capture CO2 mitigating climate change. But they are now nearing collapse.

Save Our Seas Act

Baseline Economic Situation
Fossil Fuel Production

Petroleum energy security

Government revenue from offshore drilling

Produce Negative Externalities

Severe weather causes economic loss across U.S. & global instability - poses national threat

Warming seas cannot absorb much more CO2
50% of coral reefs already lost due to warmer oceans
Massive CO2 emissions acidify oceans, bleaching corals important to combat climate change
Oil spills, tanker collisions, and seismic testing impact whale populations. Whales are ocean farmers, vital to fertilizing phytoplankton that capture carbon and release O2

Economic Opportunities

Back renewable energy: solar, wind, geothermal
Tighten whales protection that benefit all ocean systems
Invest in Maglev mass transit, creating jobs & revenue
Support thriving renewable sector/shift from oil subsidies
Replace failed mass tourism with sustainable eco-tourism
Incentivize car manufacturer to increase electric car production to keep up with global trends
Capitalize on eco-system services like the $172 billion value of coral reefs by reducing impacts
Replicate success in shifting from coal to solar
Incentivize profitable capture of methane from fossil fuels production and agriculture

Baseline Economic Situation
Plastic production

Feedstock for the economy

Cornerstone of convenience packaging

Widely dispersed throughout the economy

Produce Negative Externalities

Plastics persist for centuries while releasing harmful chemicals
Plastic particles found in human food and water
More plastic than fish in the ocean by 2050
Plastics are capable of killing all ocean species from plankton to the largest animal -blue whales
According to the American Academy of Pediatrics, plastic chemicals are harming our children endocrine systems

Economic Opportunities

Provide economic incentives to install and use "renewable" plastics generating a circular economy
R and D to improve compostable plastics and Federal tax credits for communities with industrial compost facilities
More chemical regulations on plastics
Oil subsidies reallocated to support recycling industry in the USA reducing waste and creating jobs
Provide foreign aid to developing nations to improve waste management
Negotiate better plastic waste management in international trade
Mandatory bottle bills in all 50 states will bolster economy and largely alleviate plastic pollution

Be the leader who supports cleaner technology and jobs that benefit our economy and the ocean life support system currently in peril

What are your ideas?

To learn more visit:
www.plasticoceanproject.org

Thank you
ILCSWMA