NIST National Institute of Standards and Technology
U.S. Department of Commerce

HAWAIʻI PACIFIC UNIVERSITY

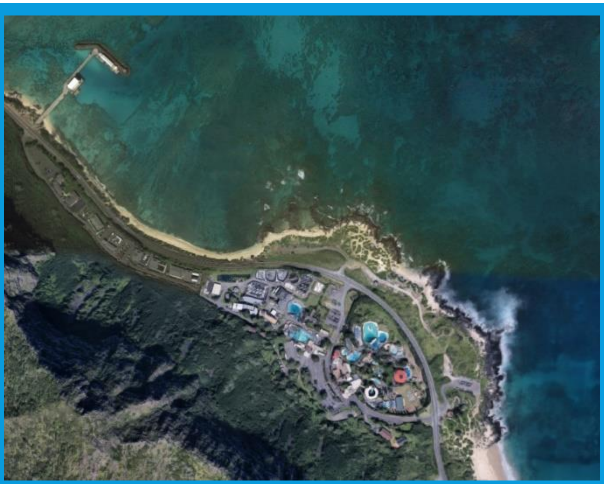
CENTER FOR MARINE DEBRIS RESEARCH

STANDARDS FOR MEASUREMENT SCIENCE OF MICROPLASTIC POLLUTION

Jennifer M. Lynch, Ph.D.

Research Biologist, Chemical Sciences Division, National Institute of Standards and Technology

Co-Director, Center for Marine Debris Research, Hawaii Pacific University



CENTER FOR MARINE DEBRIS RESEARCH

MISSION:

The Center for Marine Debris Research develops and applies optimal methods to investigate the sources, transport, fate, and impacts of plastic marine debris. The Center also disseminates this knowledge to inform management and stimulate ocean stewardship.

VISION:

The ultimate goal of all activities of the Center for Marine Debris Research is a trash-free ocean.

WHERE?

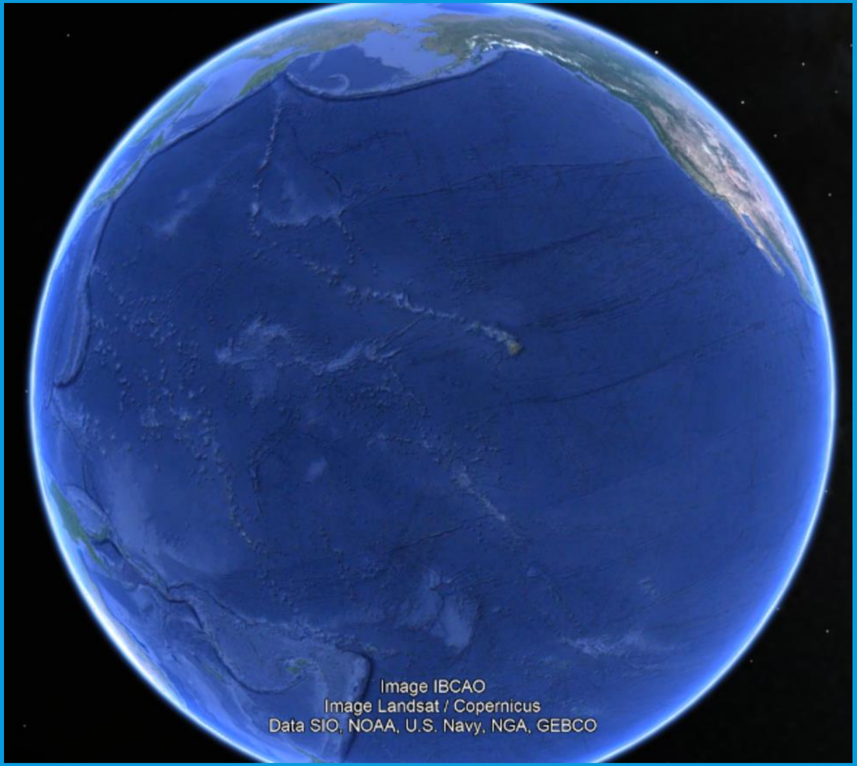
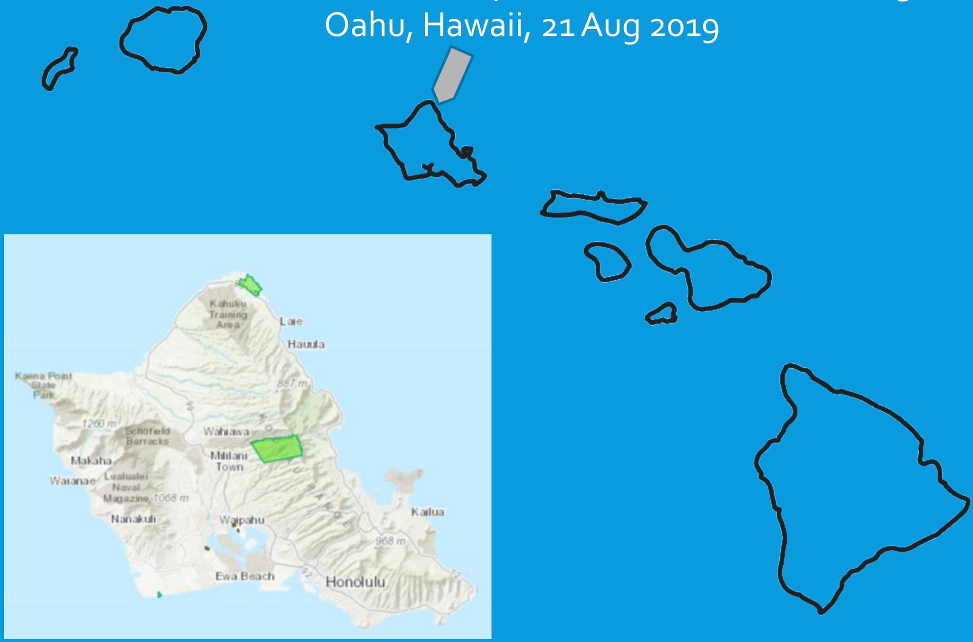


Image IBCAO
Image Landsat / Copernicus
Data SIO, NOAA, U.S. Navy, NGA, GEBCO

WHY?



James Campbell National Wildlife Refuge
Oahu, Hawaii, 21 Aug 2019

WHO?

WHEN?

2009

HPU (Hyrenbach) presents first studies on seabirds

2010

NIST and HPU's partnership begins

2013

NIST Biorepository begins collecting ingested marine debris from Pacific sea turtles

2014

HPU (Jensen and Hyrenbach) publishes polymer identification in seabirds

2017

Hawaii Marine Debris Action Plan Research Workshop

HPU and NIST (Lynch and Hyrenbach) publish 3 studies

2018

HPU and NIST establish CMDR at HPU Makapu`u campus

CMDR publishes 6 studies

CMDR submits 2 federal grant proposals

2019

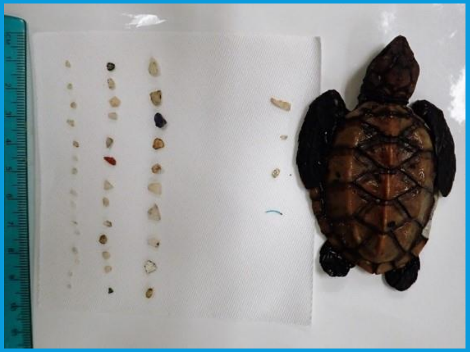
CMDR hosts HI Marine Debris Action Plan Research Workshop

CMDR publishes 1 study and submits 3 manuscripts

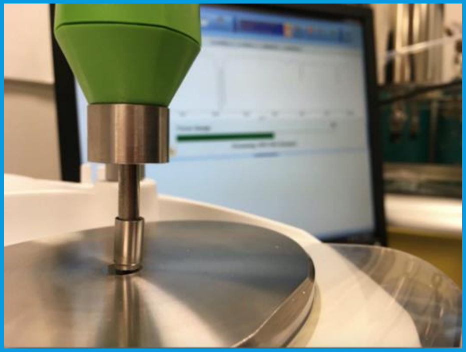
NIST awards HPU with a cooperative agreement to fund CMDR

CMDR website goes live and lab renovations begin

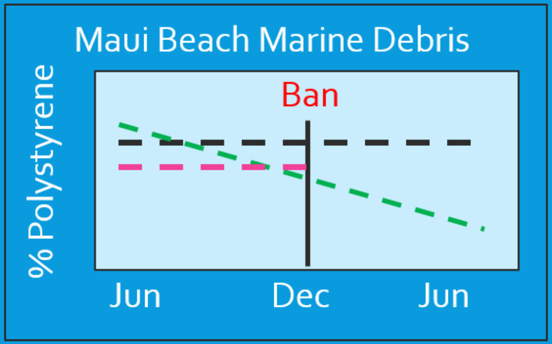
WHAT?



Biology

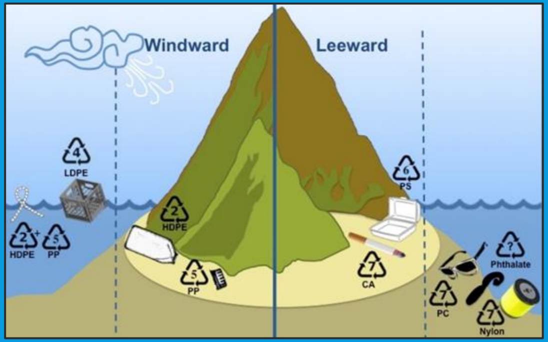


Chemistry



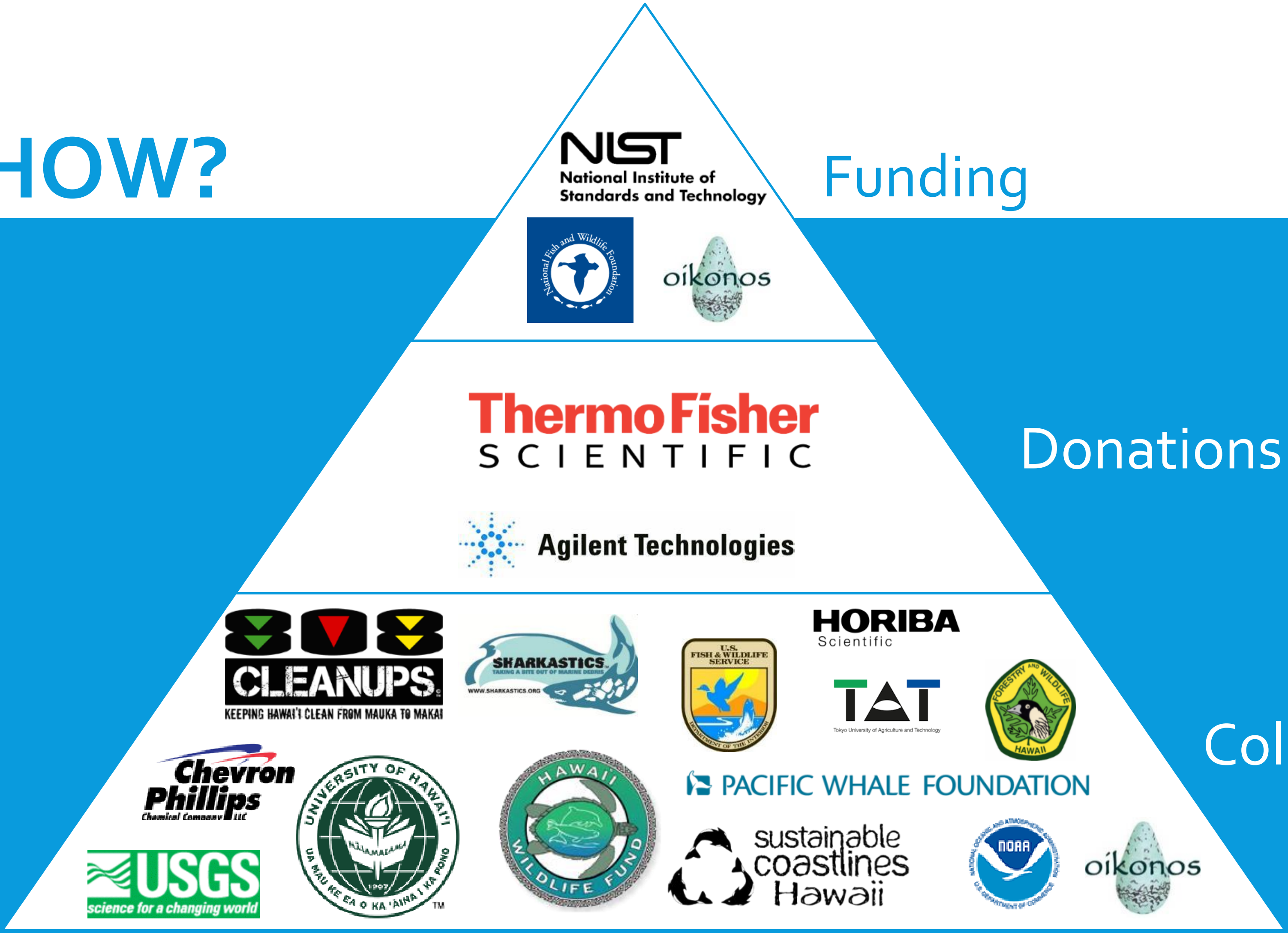
Policy and Economics

Engineering



Physics

HOW?



Funding

Donations

Collaborations

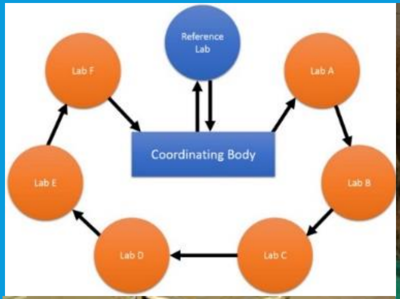
NIST'S ROLE

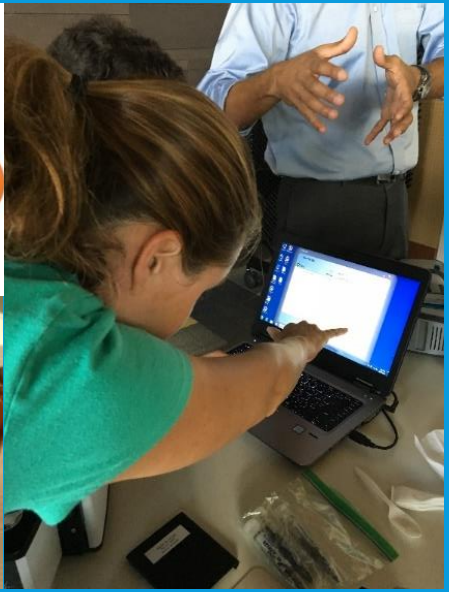
"There are limitless possibilities for NIST to be involved in the marine debris issue and there's a huge need."

-Stewart Harris

Director, Marine and Environmental Stewardship, Plastics Division, American Chemistry Council

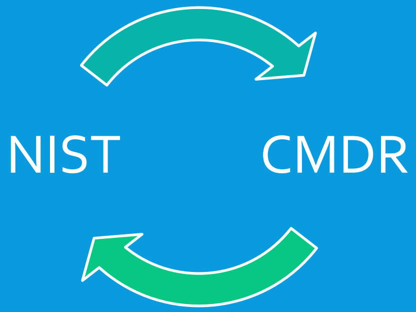
- Describe best practices
- Harmonize methods
- Produce reference materials
- Transfer measurement technologies





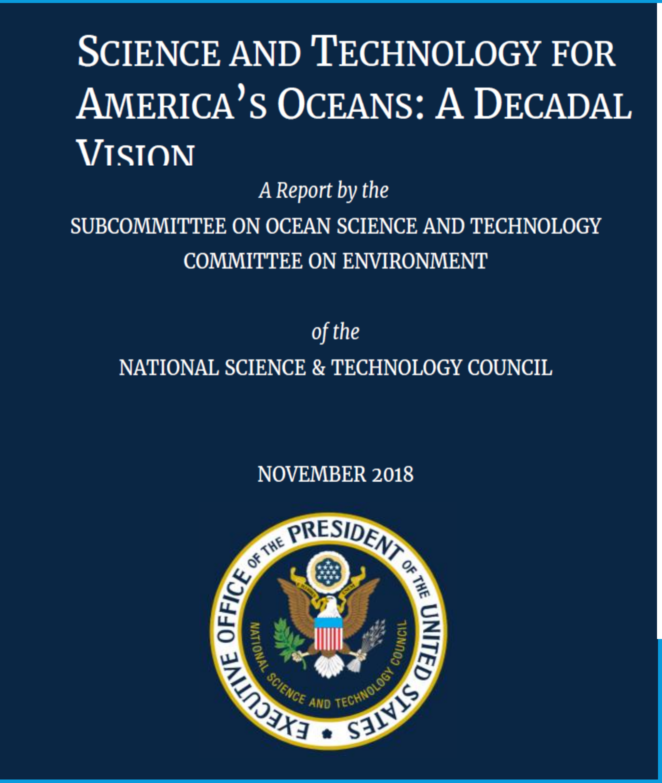
NIST – HAWAII PACIFIC UNIVERSITY PARTNERSHIP

- NIST transfers technology to CMDR to educate students on best practices
- CMDR applies best methods to answer fundamental questions
  - Sources
  - Timing of littering
  - Quantities
  - Types
  - Quantities of additives or contaminants
  - Biological effects
  - Transport and fate of debris
  - Testing effectiveness of policies or engineering
- Results inform NIST as to what standards are needed


NIST

CMDR

STANDARDIZATION & ACCURACY IS NEEDED



SCIENCE AND TECHNOLOGY FOR AMERICA'S OCEANS: A DECADAL VISION

A Report by the

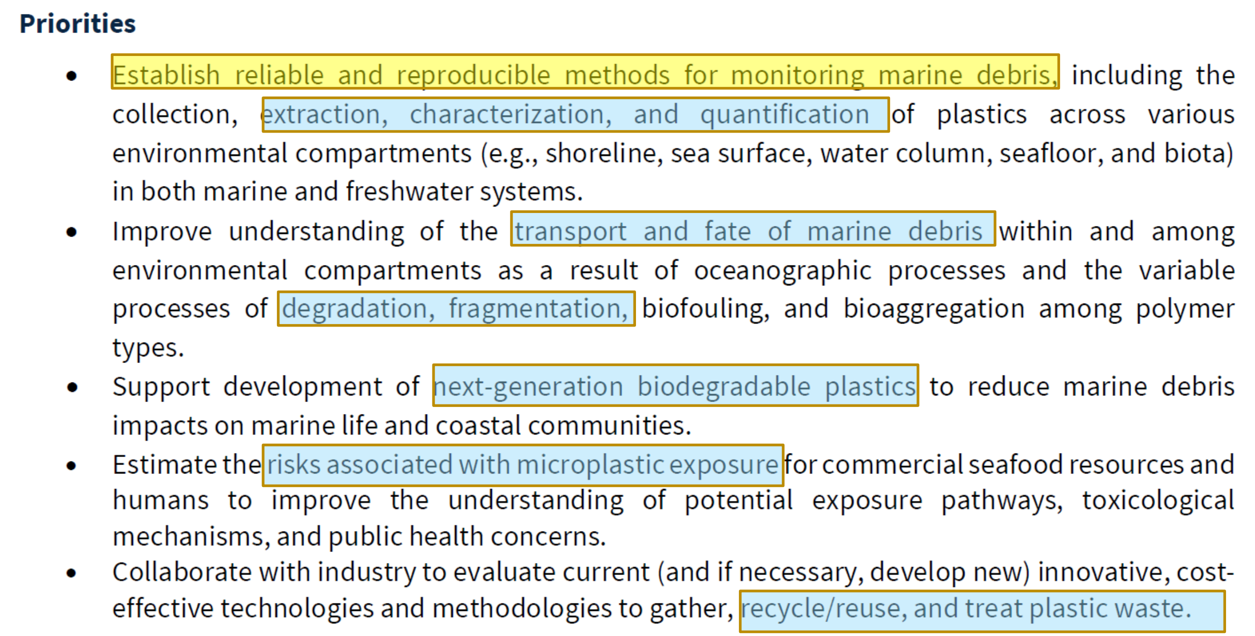
SUBCOMMITTEE ON OCEAN SCIENCE AND TECHNOLOGY

COMMITTEE ON ENVIRONMENT

of the

NATIONAL SCIENCE & TECHNOLOGY COUNCIL

NOVEMBER 2018



Priorities

- Establish reliable and reproducible methods for monitoring marine debris, including the collection, extraction, characterization, and quantification of plastics across various environmental compartments (e.g., shoreline, sea surface, water column, seafloor, and biota) in both marine and freshwater systems.
- Improve understanding of the transport and fate of marine debris within and among environmental compartments as a result of oceanographic processes and the variable processes of degradation, fragmentation, biofouling, and bioaggregation among polymer types.
- Support development of next-generation biodegradable plastics to reduce marine debris impacts on marine life and coastal communities.
- Estimate the risks associated with microplastic exposure for commercial seafood resources and humans to improve the understanding of potential exposure pathways, toxicological mechanisms, and public health concerns.
- Collaborate with industry to evaluate current (and if necessary, develop new) innovative, cost-effective technologies and methodologies to gather, recycle/reuse, and treat plastic waste.

STANDARDIZATION & ACCURACY IS NEEDED

- Compare across studies
  - Monitor spatial and temporal trends
- Assess risk
- Inform policies
  - Monitor effectiveness of single-use item bans, recycling changes
  - Meet water quality standards

MEASUREMENT CHALLENGES

- Wide range of particle sizes (nm to m)
- Expanding diversity of polymers and additives
- Isolation of polymers from complex environmental matrices
- Rapidly evolving detection technology
- Background contamination
- Few polymer standards
- Little to no reference materials

THREE STUDIES

- Sea turtles
- Beach debris
- Larval fish

THREE STAGES NEEDING STANDARDIZATION

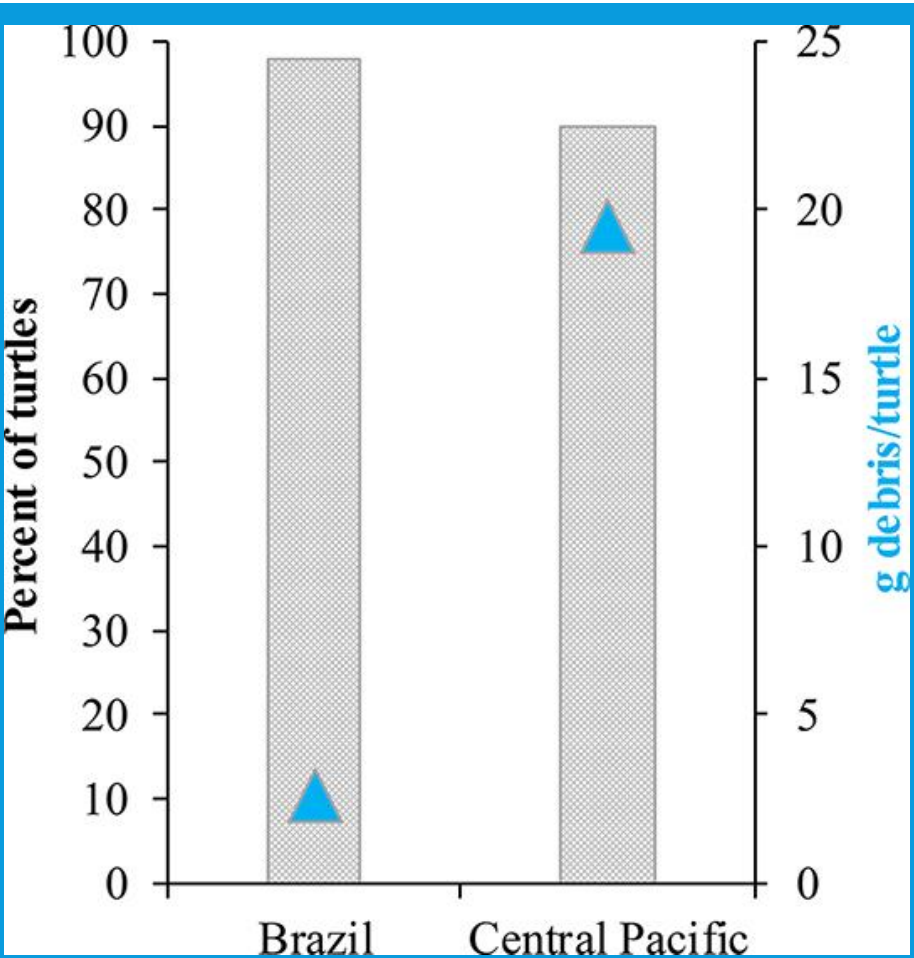
- Sample preparation
- Polymer characterization
- Data reporting (units units units!)

SEA TURTLES INGEST A LOT OF PLASTIC

Clukey et al. 2017 Mar Pollut Bull

BEST REPORTING UNITS

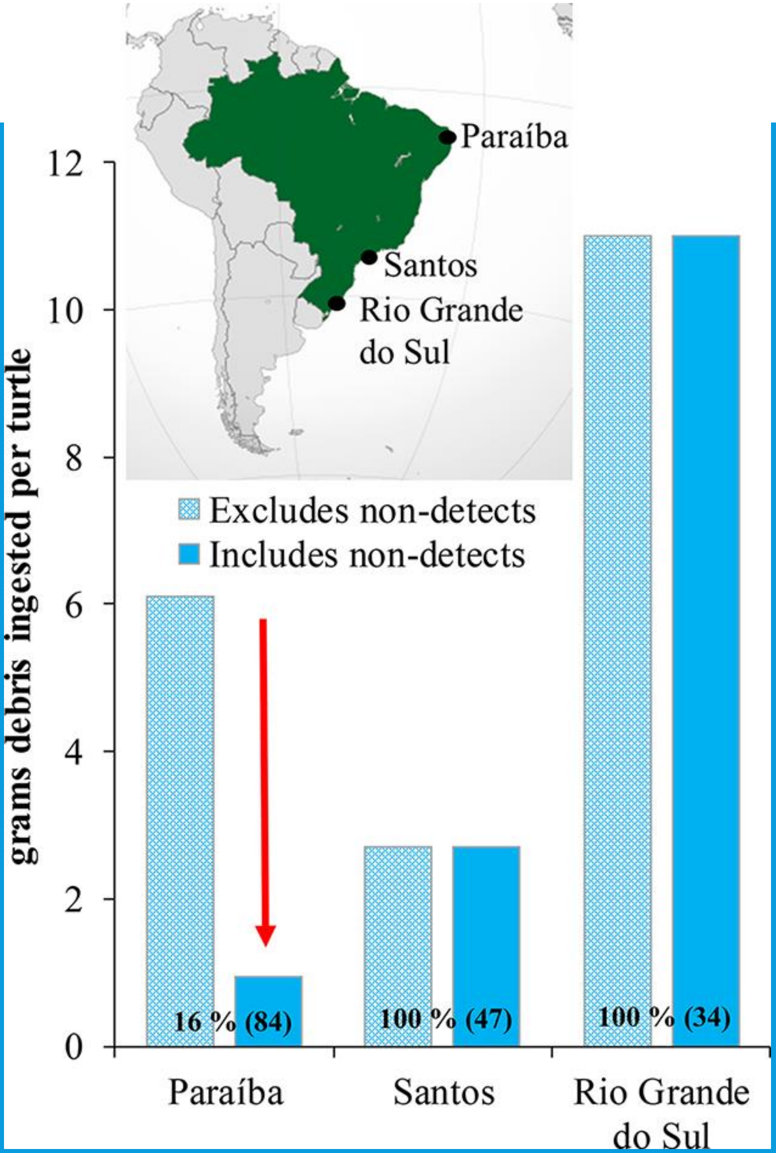
- Quantities are better than percent occurrence
- Include non-detects
- Report both particle counts and mass of polymers
- g/kg is best unit for biota



Lynch 2018 ES&T

BEST REPORTING UNITS

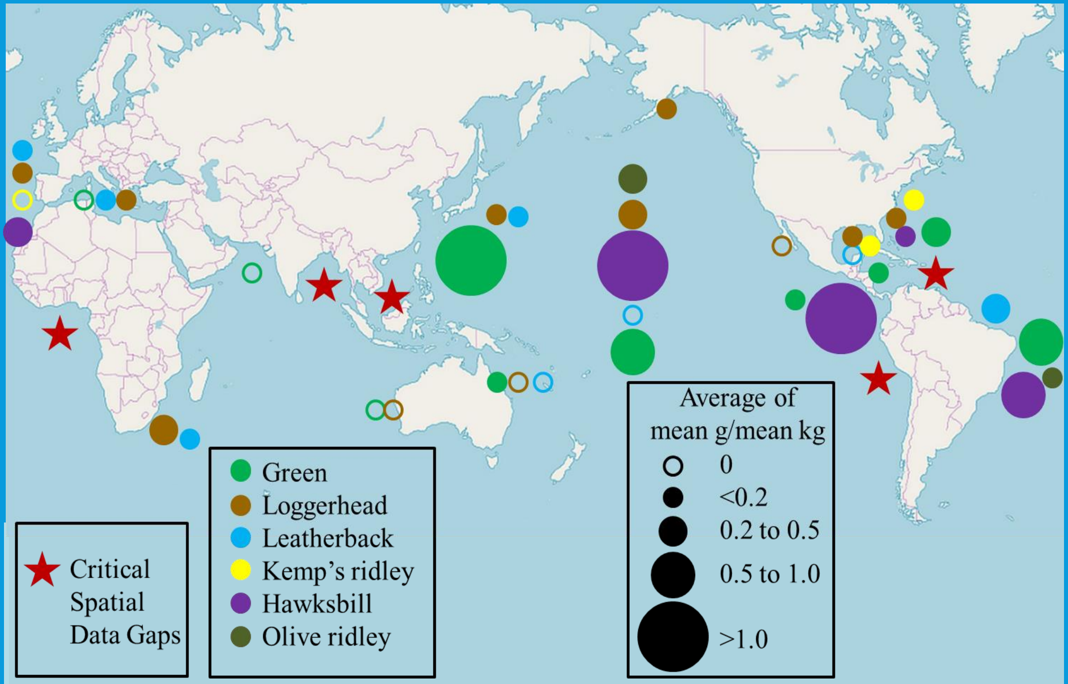
- Quantities are better than percent occurrence
- <u>Include non-detects</u>
- Report both particle counts and mass of polymers
- g/kg is best unit for biota



Lynch 2018 ES&T

BEST REPORTING UNITS

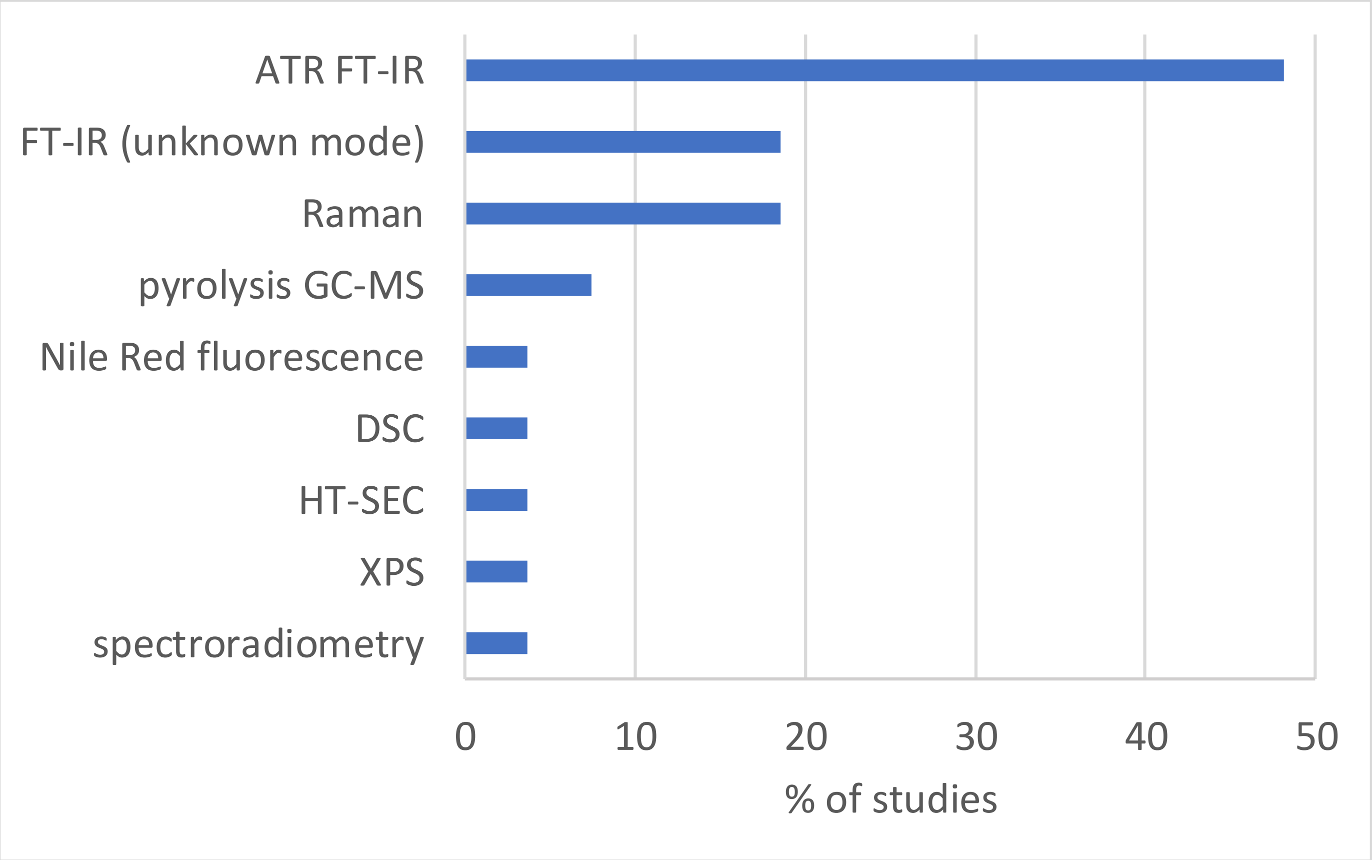
- Quantities are better than percent occurrence
- Include non-detects
- Report both particle counts and mass of polymers
- g/kg is best unit for biota



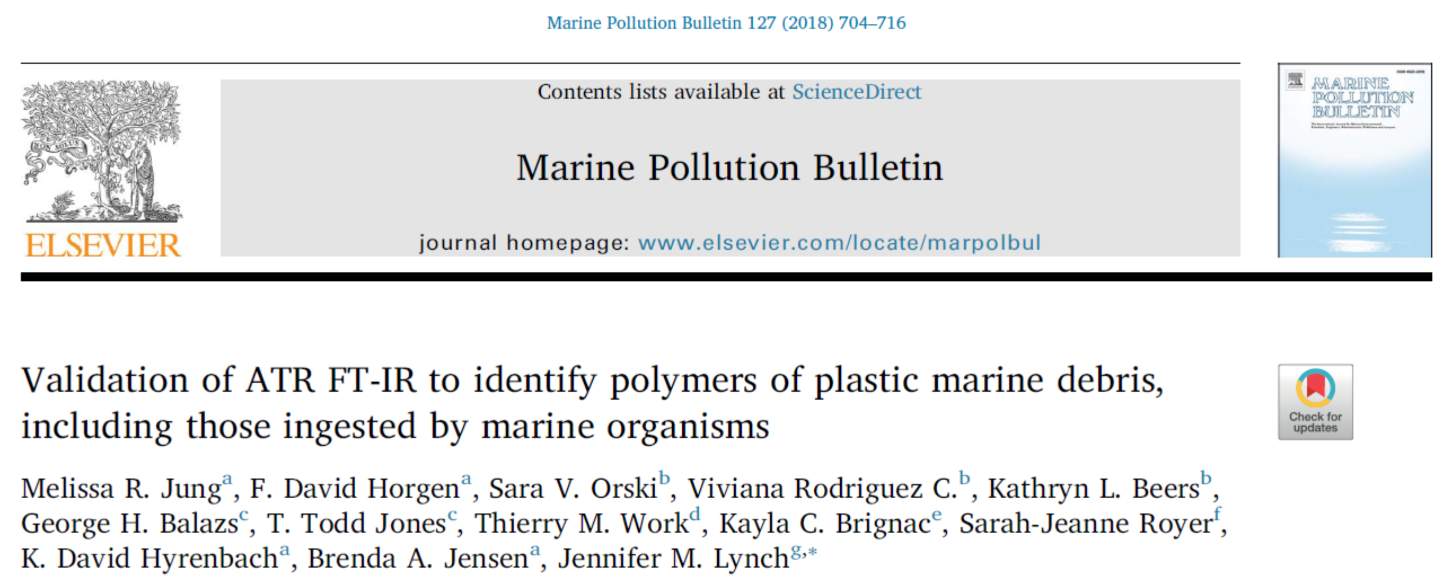
Lynch 2018 ES&T

POLYMER IDENTIFICATION METHODS

Google Scholar search on Aug 24, 2019, for "Polymer identification marine debris" since 2018. Top 27 hits of only primary sources



POLYMER IDENTIFICATION METHODS



Marine Pollution Bulletin 127 (2018) 704–716

Contents lists available at ScienceDirect

ELSEVIER

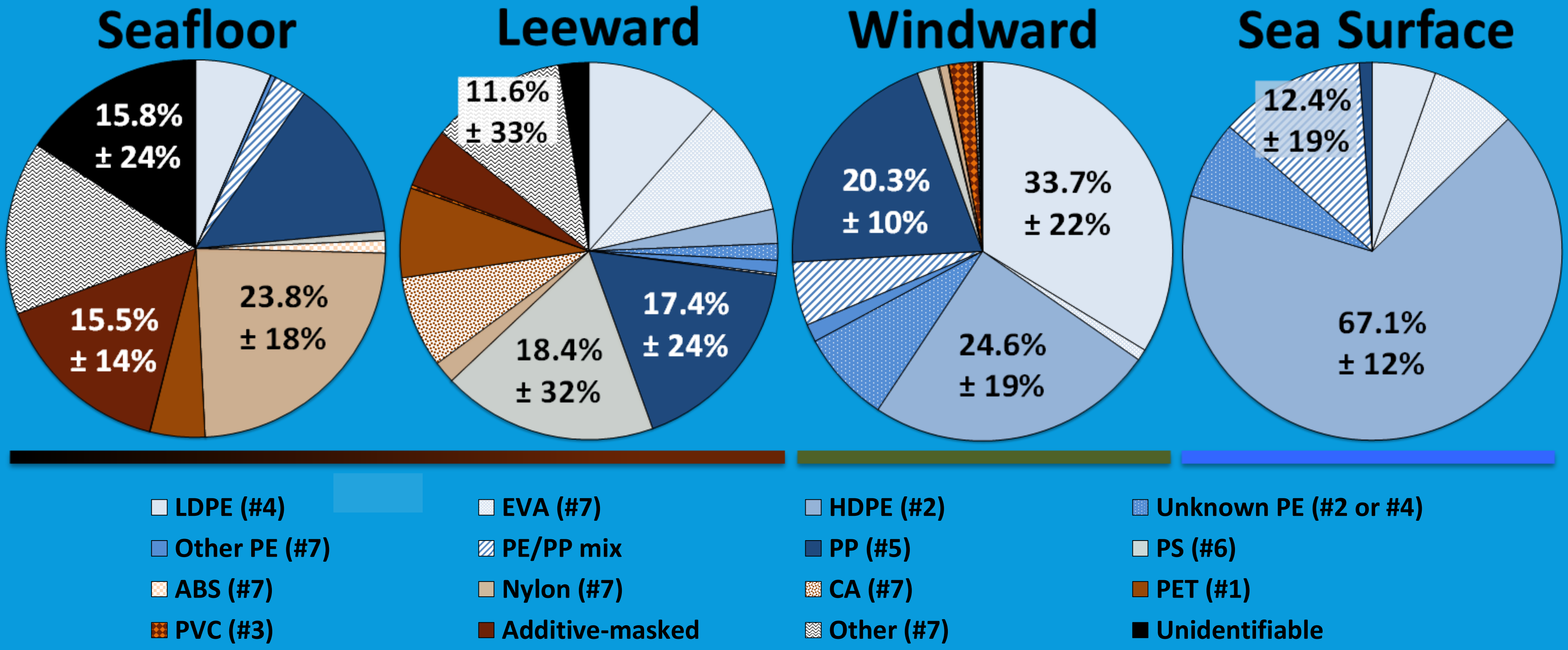
Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Validation of ATR FT-IR to identify polymers of plastic marine debris, including those ingested by marine organisms

Melissa R. Jung[a], F. David Horgen[a], Sara V. Orski[b], Viviana Rodriguez C.[b], Kathryn L. Beers[b], George H. Balazs[c], T. Todd Jones[c], Thierry M. Work[d], Kayla C. Brignac[e], Sarah-Jeanne Royer[f], K. David Hyrenbach[a], Brenda A. Jensen[a], Jennifer M. Lynch[g,*]

BEACH DEBRIS POLYMER COMPOSITION

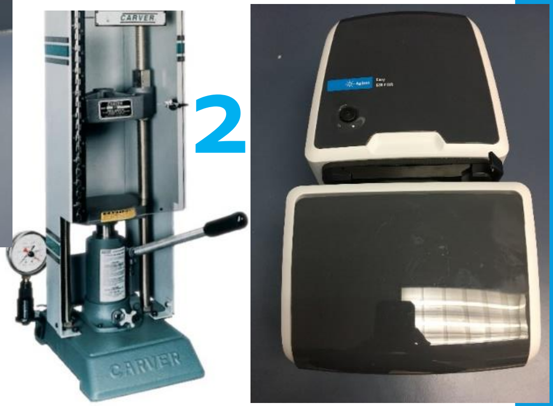


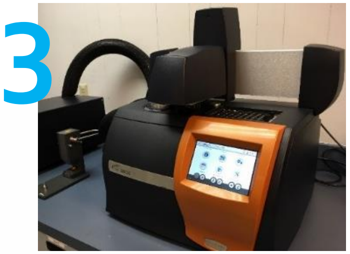
Brignac et al. in press ES&T

FOUR-STEP WORKFLOW

Chevron Phillips Chemical Company LLC


1

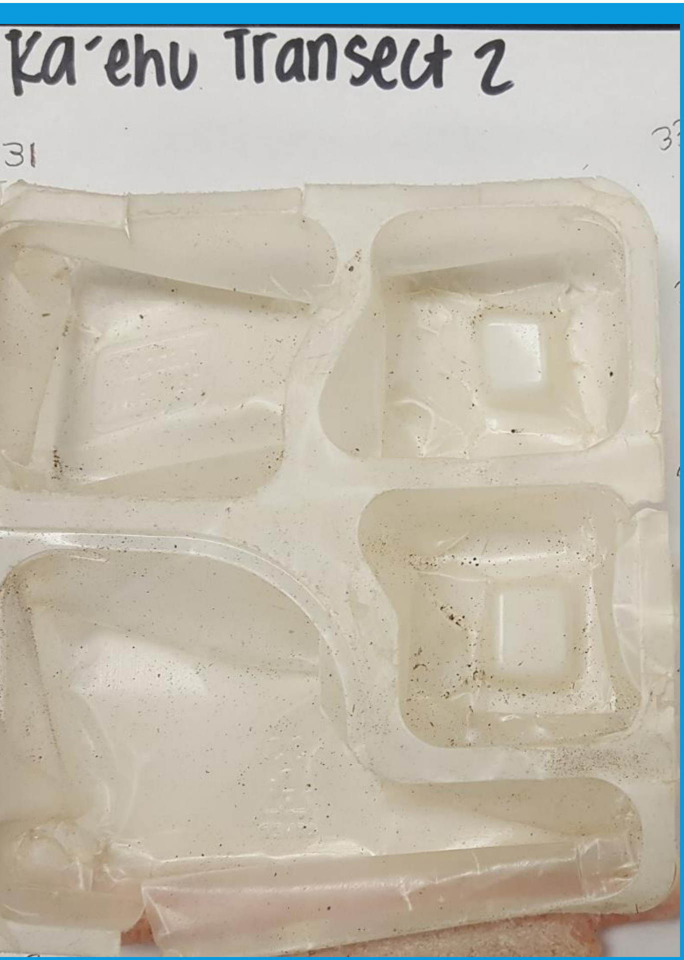

2


3

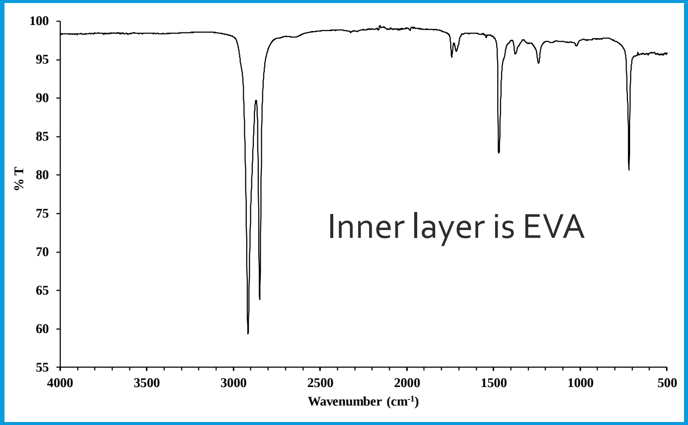

4

1. ATR FT-IR
2. FT-IR total transmission of thin film
3. Differential Scanning Calorimetry
4. Optical or FT-IR microscopy of cross sections

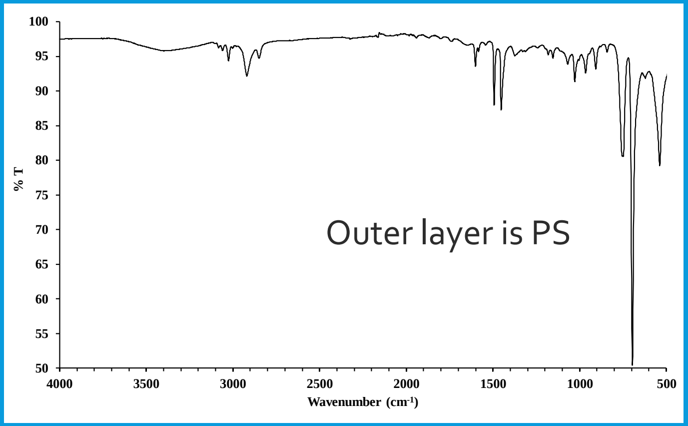
EXAMPLE – FOUR-STEP WORKFLOW



1. ATR FT-IR
2. FT-IR total transmission of thin film
3. Differential Scanning Calorimetry
4. Optical or FT-IR microscopy of cross sections

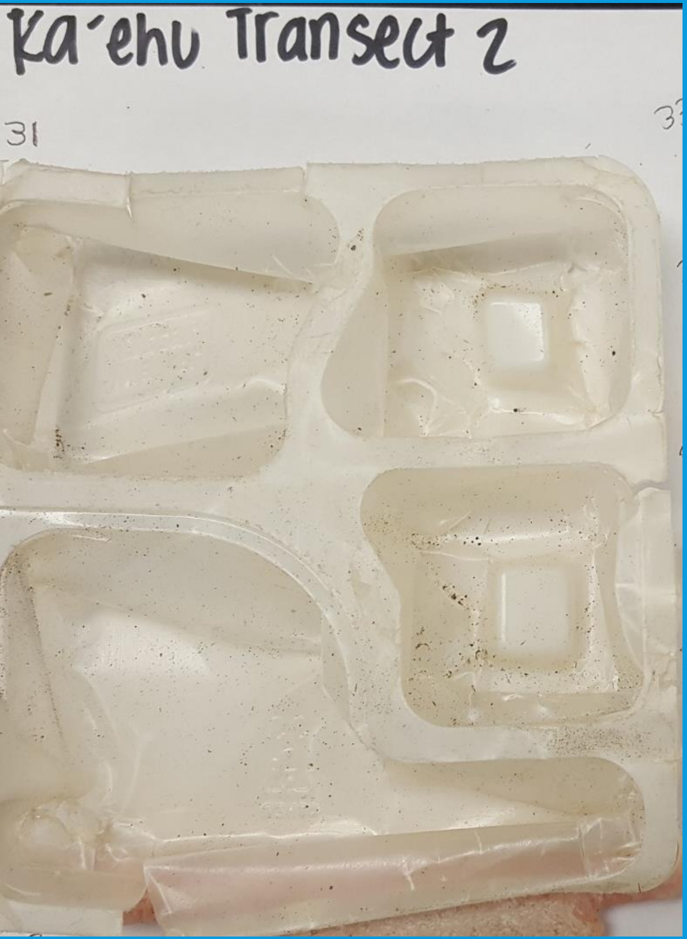


Inner layer is EVA



Outer layer is PS

EXAMPLE – FOUR-STEP WORKFLOW

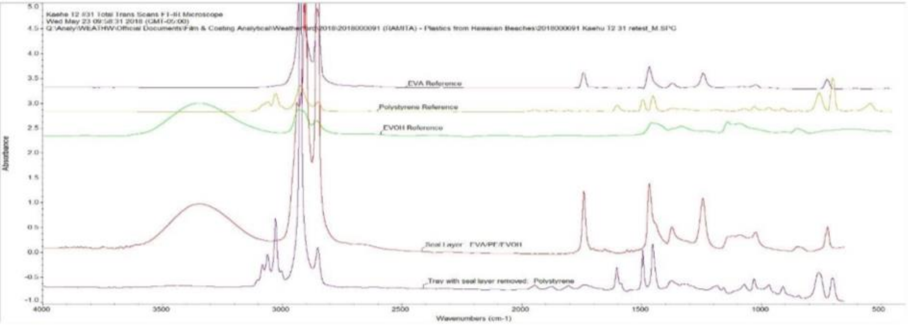


1. ATR FT-IR

   Inner layer is EVA; outer layer is PS

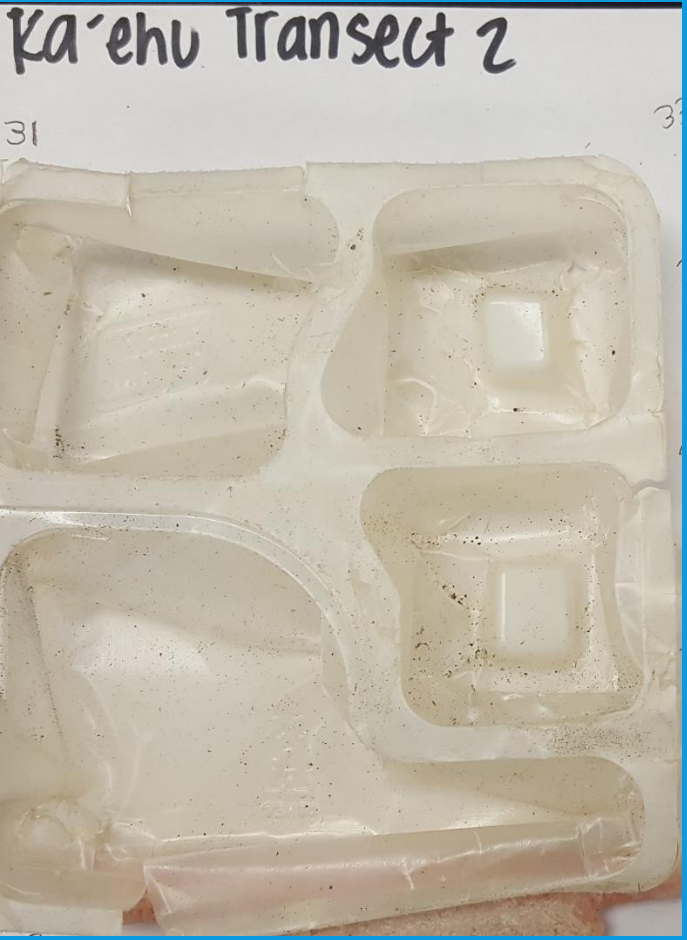
2. FT-IR total transmission of thin film

   Inner layer is PE/EVA/EVOH ; outer layer is PS

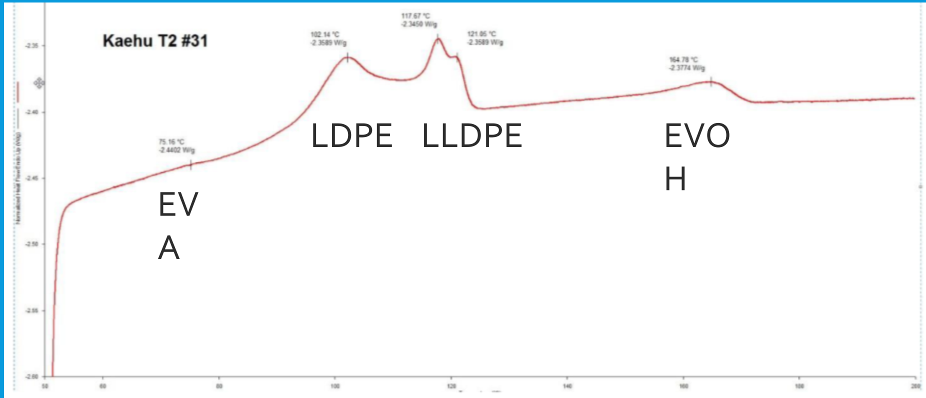


3. Differential Scanning Calorimetry
4. Optical or FT-IR microscopy of cross sections

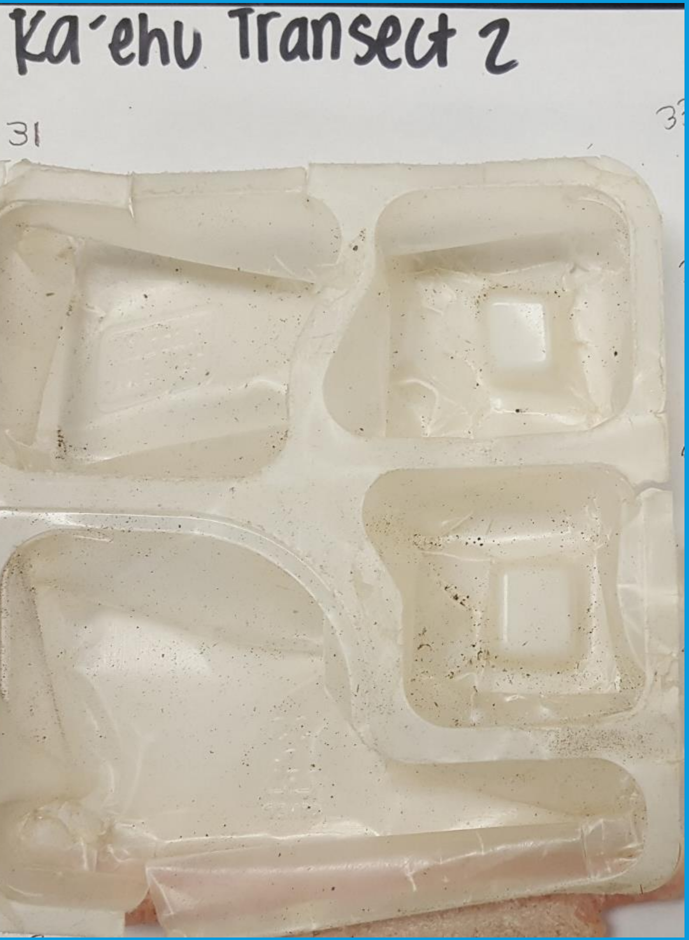
EXAMPLE – FOUR-STEP WORKFLOW



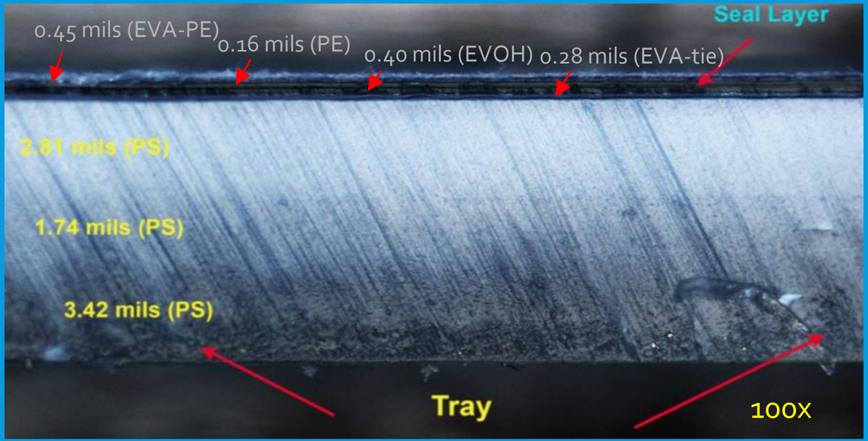
1. ATR FT-IR	Inner layer is EVA; outer layer is PS
2. FT-IR total transmission of thin film	Inner layer is PE/EVA/EVOH ; outer layer is PS
3. Differential Scanning Calorimetry	23-25% EVA/LDPE/LLDPE/EVOH (cannot see PS)
4. Optical or FT-IR microscopy of cross sections	



EXAMPLE – FOUR-STEP WORKFLOW



1. ATR FT-IR	Inner layer is EVA; outer layer is PS
2. FT-IR total transmission of thin film	Inner layer is PE/EVA/EVOH ; outer layer is PS
3. Differential Scanning Calorimetry	23-25% EVA/LDPE/LLDPE/EVOH (cannot see PS)
4. Optical or FT-IR microscopy of cross sections	

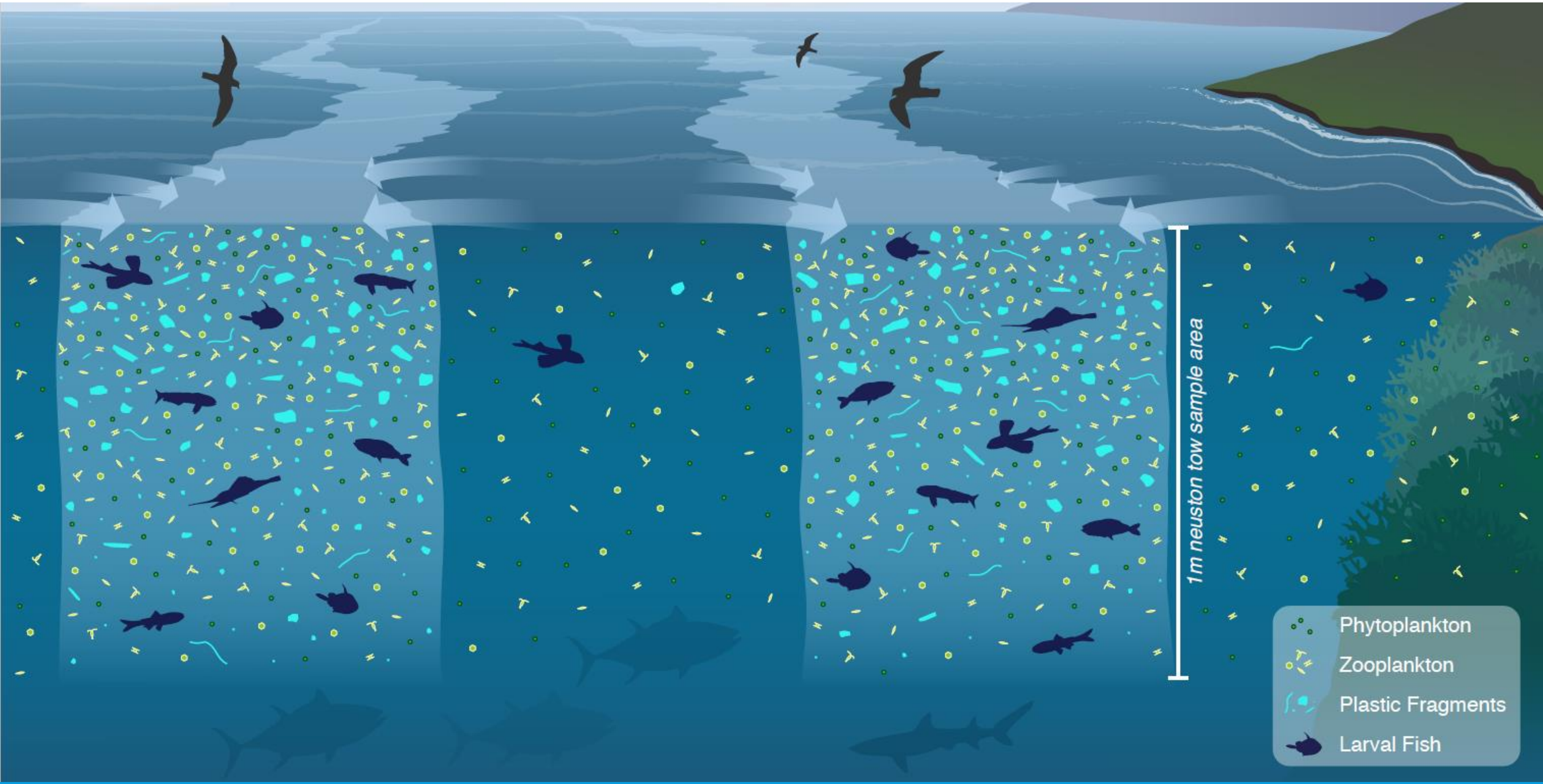


FOUR-STEP WORKFLOW REVEALED…

- 8 % of HI beach debris items were multi-layer composites
- 63 % (15 / 24) of HI beach debris items were made of multiple polymers
- 11 of those (73 %) were not revealed by ATR FT-IR alone
- Multiple methods are required

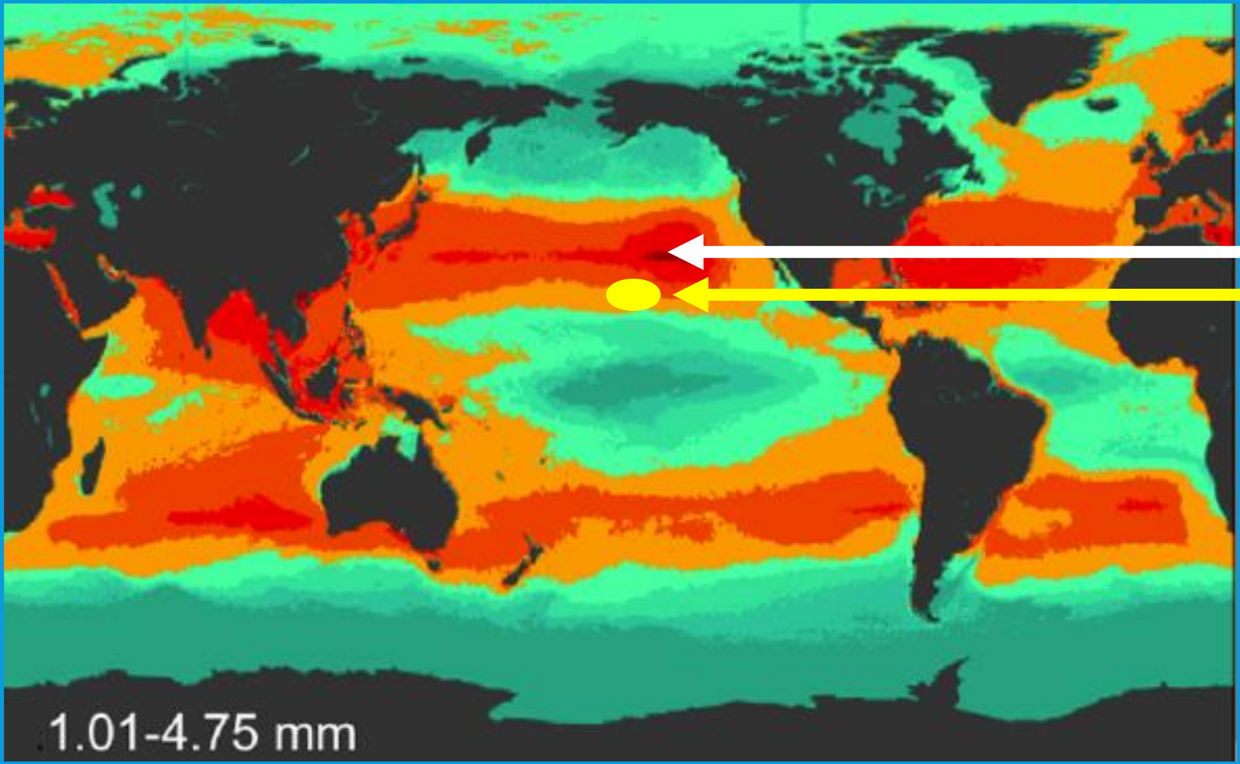
Lynch et al. in prep.

LARVAL FISH



Gove & Whitney et al. in press PNAS

HAWAII SEA SURFACE (pieces/km²)



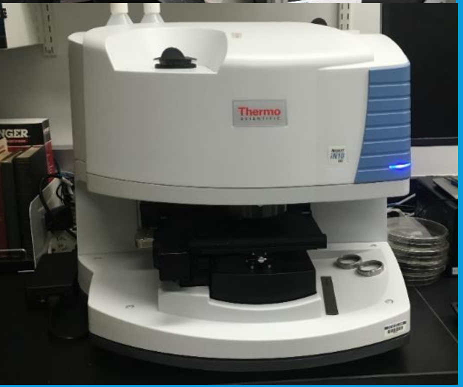
1 million

2.3 - 3.5 million

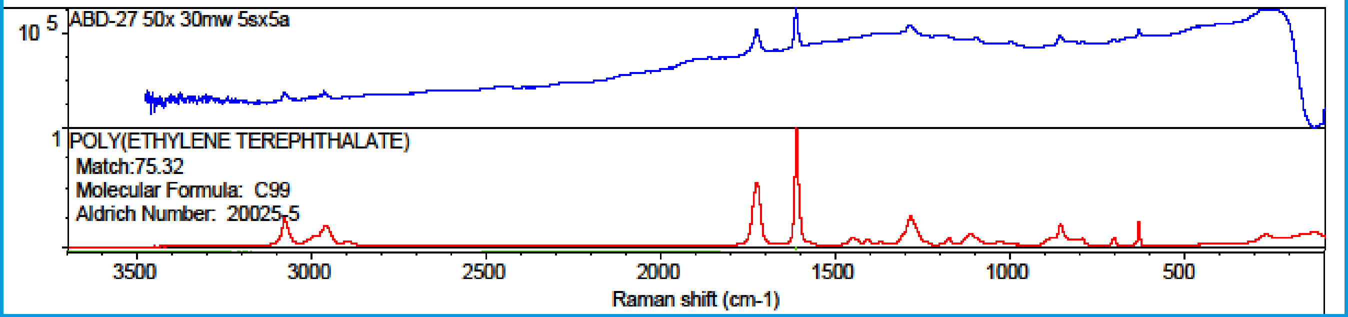
Eriksen et al. 2014

Gove & Whitney et al. in press PNAS

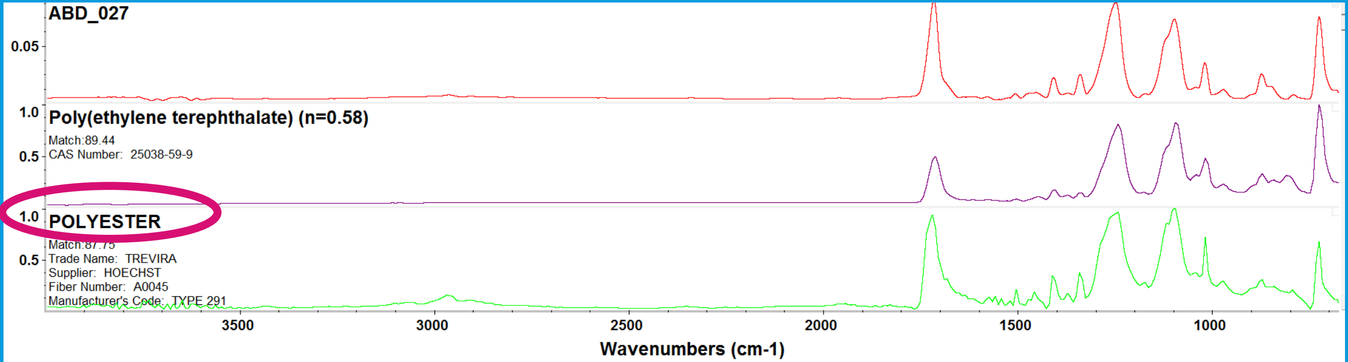
LARVAL FISH INGEST MICROFIBERS



Raman

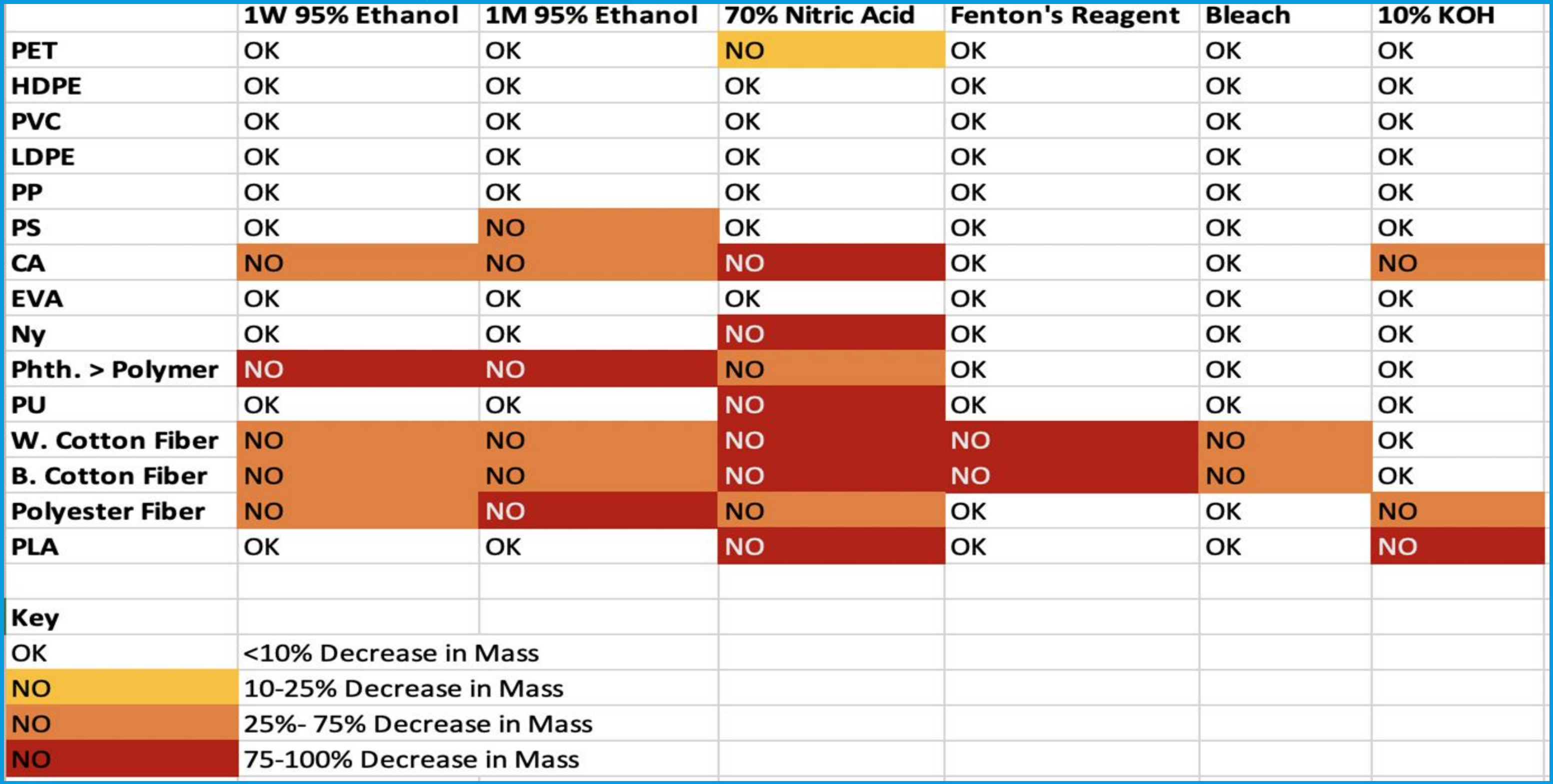


FT-IR



Gove & Whitney et al. in press PNAS

CHEMICAL COMPATIBILITY OF FISH DIGESTION METHODS



	1W 95% Ethanol	1M 95% Ethanol	70% Nitric Acid	Fenton's Reagent	Bleach	10% KOH
PET	OK	OK	NO	OK	OK	OK
HDPE	OK	OK	OK	OK	OK	OK
PVC	OK	OK	OK	OK	OK	OK
LDPE	OK	OK	OK	OK	OK	OK
PP	OK	OK	OK	OK	OK	OK
PS	OK	NO	OK	OK	OK	OK
CA	NO	NO	NO	OK	OK	NO
EVA	OK	OK	OK	OK	OK	OK
Ny	OK	OK	NO	OK	OK	OK
Phth. > Polymer	NO	NO	NO	OK	OK	OK
PU	OK	OK	NO	OK	OK	OK
W. Cotton Fiber	NO	NO	NO	NO	NO	OK
B. Cotton Fiber	NO	NO	NO	NO	NO	OK
Polyester Fiber	NO	NO	NO	OK	OK	NO
PLA	OK	OK	NO	OK	OK	NO
Key						
OK	<10% Decrease in Mass					
NO	10-25% Decrease in Mass					
NO	25%- 75% Decrease in Mass					
NO	75-100% Decrease in Mass					

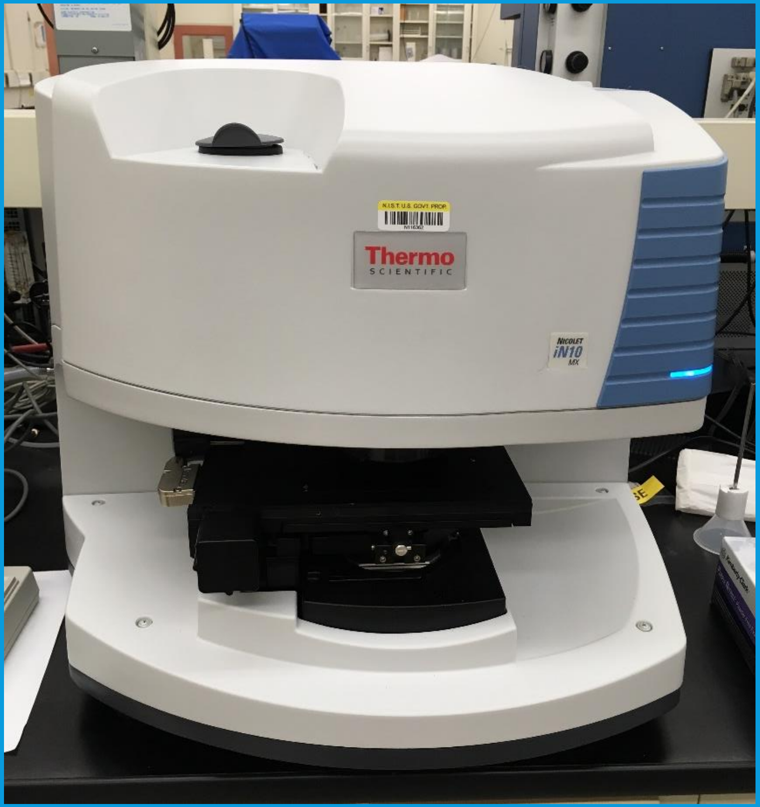
Karr et al. in prep.

NIST'S CAPABILITIES

- Environmental chemistry
- Polymer science
- Material weathering
- Polymer and environmental SRMs
- Cryohomogenization reference material production facility
- Inter-laboratory comparisons
- Circular Economy Initiative (Kathryn Beers)

NIST'S CAPABILITIES

- Environmental chemistry
- Polymer science
- Material weathering
- Polymer and environmental SRMs
- Cryohomogenization reference material production facility
- Inter-laboratory comparisons
- Circular Economy Initiative (Kathryn Beers)



NIST'S CAPABILITIES

- Environmental chemistry
- Polymer science
- Material weathering
- Polymer and environmental SRMs
- Cryohomogenization reference material production facility
- Inter-laboratory comparisons
- Circular Economy Initiative (Kathryn Beers)

NIST'S CAPABILITIES

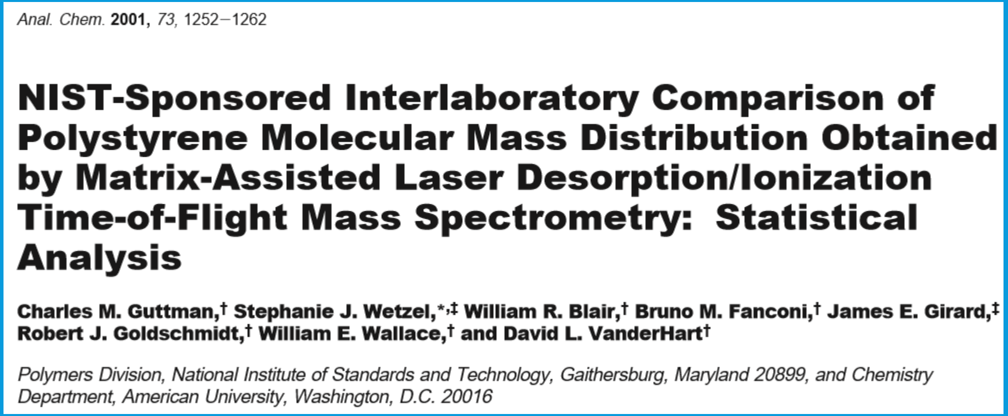
- Environmental chemistry
- Polymer science
- Material weathering
- Polymer and environmental SRMs
- Cryohomogenization reference material production facility
- Inter-laboratory comparisons
- Circular Economy Initiative (Kathryn Beers)

NIST'S CAPABILITIES

- Environmental chemistry
- Polymer science
- Material weathering
- Polymer and environmental SRMs
- Cryohomogenization reference material production facility
- Inter-laboratory comparisons
- Circular Economy Initiative (Kathryn Beers)

NIST'S CAPABILITIES/FACILITIES

- Environmental chemistry
- Polymer science
- Material weathering
- Polymer and environmental SRMs
- Cryohomogenization reference material production facility
- Inter-laboratory comparisons
- Circular Economy Initiative (Kathryn Beers)



Anal. Chem. **2001,** *73,* 1252–1262

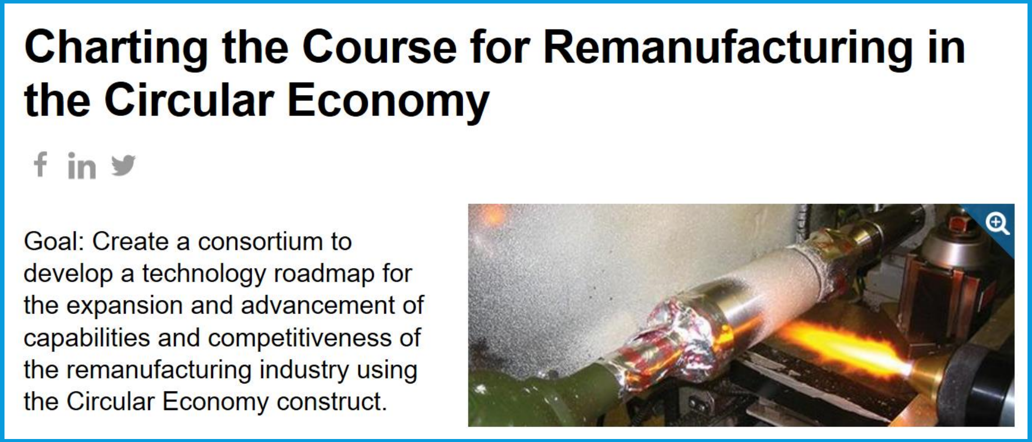
NIST-Sponsored Interlaboratory Comparison of Polystyrene Molecular Mass Distribution Obtained by Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry: Statistical Analysis

Charles M. Guttman,[†] Stephanie J. Wetzel,[*,‡] William R. Blair,[†] Bruno M. Fanconi,[†] James E. Girard,[‡] Robert J. Goldschmidt,[†] William E. Wallace,[†] and David L. VanderHart[†]

Polymers Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, and Chemistry Department, American University, Washington, D.C. 20016

NIST'S CAPABILITIES

- Environmental chemistry
- Polymer science
- Material weathering
- Polymer and environmental SRMs
- Cryohomogenization reference material production facility
- Inter-laboratory comparisons
- **Circular Economy Initiative (Kathryn Beers)**



Charting the Course for Remanufacturing in the Circular Economy

Goal: Create a consortium to develop a technology roadmap for the expansion and advancement of capabilities and competitiveness of the remanufacturing industry using the Circular Economy construct.

NIST POLYMER SRMs

At least 27 consisting of 7 polymers

Main polymer	SRM	Description
HDPE	1483a	Linear Polyethylene
HDPE	1484a	Linear Polyethylene
LDPE	1473c	Low Density Polyethylene Resin
LDPE	1476a	Branched Polyethylene Resin
PE	1474b	Polyethylene Resin
PE	1482a	Linear Polyethylene Narrow Molecular Mass Distribution (Nominal Mass-Average Molar Mass of 32 100 g/mol)
PE	1496	Unpigmented Polyethylene Gas Pipe Resin
PE	2855	Additive Elements in Polyethylene
PE	2885	Polyethylene (Mw, 6 280 g/mol)
PE	2887	Polyethylene (Mw, 196 400 g/mol)
PE	8540	IAEA-CH-7 (Carbon and Hydrogen Isotopes in Polyethylene Foil)
PMMA	1487	Poly(Methyl Methacrylate) (6 K Narrow Molecular Weight Distribution)
PMMA	1488	Poly (Methyl Methacrylate) 29 K Narrow Molecular Weight Distribution
PS	705a	Polystyrene (Narrow Molecular Weight Distribution)
PS	706a	Polystyrene (Broad Molecular Mass Distribution)
PS	1453	Thermal Conductivity - Expanded Polystyrene Board
PS	1478	Polystyrene (Narrow Molecular Weight Distribution)
PS	1479	Polystyrene (Narrow Molecular Weight Distribution)
PS	1691	Polystyrene Spheres (Nominal Diameter 0.3 µm)
PS	1961	Polystyrene Spheres 30 µm Diameter Polystyrene Spheres
PS	1965	Microsphere Slide (10-µm Polystyrene Spheres)
PS	2870	Relative Permittivity and Loss Tangent 1422 Cross-Linked Polystyrene
PS	2881	Polystyrene Absolute Molecular Mass Distribution Standard
PVC	2859	Restricted Elements in Polyvinyl Chloride
PVC	2860	Phthalates in Polyvinyl Chloride
PVC	2861	Restricted Elements in Polyvinyl Chloride
ETFE	8634	Ethylene Tetrafluoroethylene for Particle Size Distribution and Morphology
PLC	8394	Tissue Engineering Reference Scaffolds for Cell Culture

NIST ENVIRONMENTAL SRMs

4 matrices never tested for plastic particles

Matrix	SRM	Description
Dust	2584	Trace Elements in Indoor Dust (Nominal Mass Fraction of 1 % Lead)
Dust	2585	Organic Contaminants in House Dust
Dust	8632	Ultra Fine Test Dust (UFTD)
Dust	8785	Air Particulate Matter on Filter Media
Dust	8786	Filter Blank for RM 8785
Dust	1649b	Urban Dust
Sediment	1944	New York/New Jersey Waterway Sediment
Sediment	2702	Inorganics in Marine Sediment
Sediment	2703	Sediment for Solid Sampling (Small Sample) Analytical Techniques
Sediment	8704	Buffalo River Sediment
Sediment	1646a	Estuarine Sediment
Sediment	1941b	Organics in Marine Sediment
Sludge	2781	Domestic Sludge
Sludge	2782	Industrial Sludge
Soil	2587	Trace Elements in Soil Containing Lead from Paint (Nominal Mass Fraction of 3000 mg/kg Lead)
Soil	2709a	San Joaquin Soil Baseline Trace Element Concentrations

REFERENCE MATERIAL IDEAS

1. Kit of 25-50 different polymer nurdles/coupons

2. Cryogrind polymers to specific particle sizes

3. Quantify and characterize microplastic particles in existing environmental SRMs

THANK YOU!

- John Kucklick, Rebecca Pugh, Kate Beers, Sara Orski, Katy Shaw
- Brenda Jensen, David Hyrenbach, Melissa Jung, Kayla Brignac, Kathleen Page, David Horgen, Jenna Karr
- Rachel Sandquist, Ashok Deshpande, Nigel Lascelles, Dante Freeman, Davielle Drayton, Jon Whitney, Jamie Gove, Jana Phipps, George Balazs, T. Todd Jones, Shandell Brunson
- Thierry Work
- Wanda Weatherford, Ron Abbott, Rick Wagner
- Bridget O'Donnell
- Suja Sukumaran
- Ray Aivazian, Sarah-Jeanne Royer, Jim Potemra, Nikolai Maximenko, Anupam Misra, Lloyd Hihara, Jan Kealoha, Katharine Clukey
- Cheryl King, Jens Currie, Megan Lamson, Lauren Blickley, Kahi Paccaro, Fawn Leibengood, Hank Lynch

FOLLOW US

CENTER FOR MARINE DEBRIS RESEARCH

Website: www.hpu.edu/cncs/cmdr

@MarineDebrisResearch

@debrisresearch

@company/center-for-marine-debris-research