Characterization of Microplastics using Fourier Transform Infrared Spectroscopy (FT-IR)

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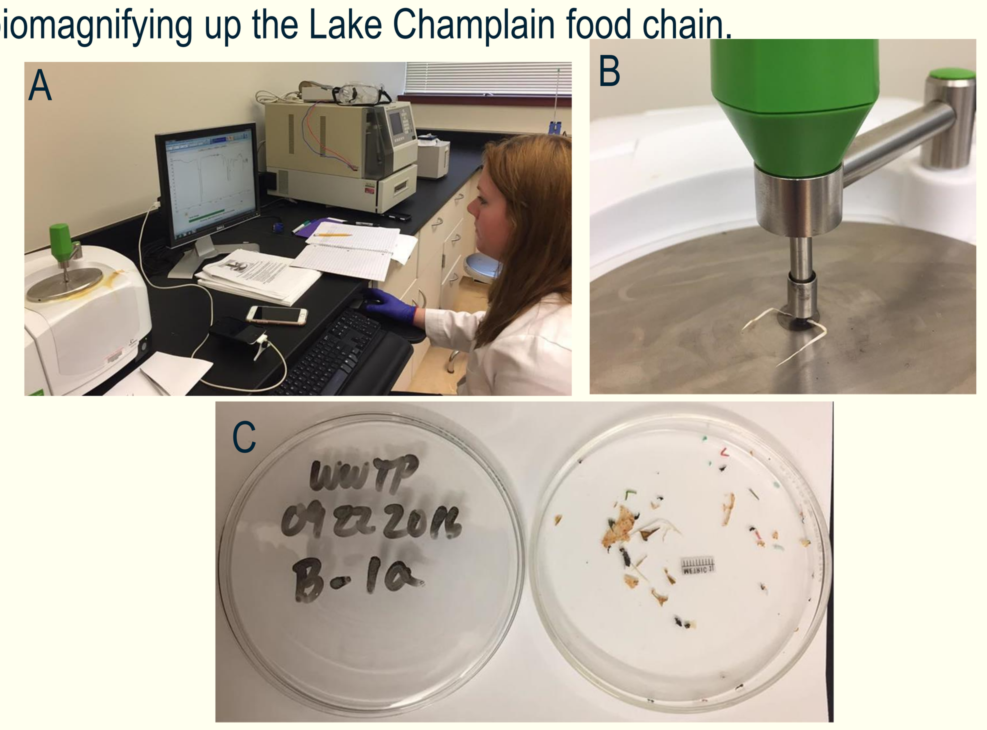
Microplastics

- Microplastics are small particles of plastic <5mm and are characterized by color, type (e.g., fragment, pellet/bead, fiber, foam, film), and density. Microplastics originate from marine debris (netting, lines, ropes), mechanical and photodegradation of macroplastics, wastewater treatment effluent (Mason et al. 2016), and have the potential to biomagnify up aquatic food webs (Raphael et al. 2013).
- These synthetic particulate adsorb contaminants and chemicals which bioaccumulate within organisms. As microplastic pollution awareness rises, scientists are characterizing, quantifying, and mapping distribution of these particulate.
- In order to determine long-term health impacts and adsorptive properties of these particles, the chemical composition must first be determined.

FT-IR

- FT-IR characterizes particles by identifying the chemical bonds in a molecule by obtaining an infrared spectrum of absorption, emission, and photoconductivity of a solid, liquid, or gas (Tagg et al. 2015).
- FT-IR detects molecular functional groups while characterizing covalent bond formation, which is cross-referenced to plastics/fiber libraries for polymetric verification.
- FT-IR has been successful at identifying plastic and rubber polymers in previous studies (Chakraborty et al. 2007).
- Lusher et al. (2013) found that of the particles characterized by FT-IR, 68% of the microplastics in fish were fibers, specifically rayon, polyester, and polyamide origins.
- Plastics pose a major health concern as they have the potential to adsorb hormone disruptors and heavy metals, like copper (Cu) and zinc (Zn). These heavy metals are highly toxic to organisms as they bioaccumulate in tissues. This bioaccumulation in tissues reported similar results (Vinodhini and Narayan, 2008). On-going SUNY Plattsburgh research on double-crested cormorants, 14 species of fish, and several invertebrate species confirms that microplastics are biomagnifying up the Lake Champlain food chain.



Figs. 1. A) Perkin Elmer FT-IR machine connected to a PC, **B)** FT-IR of a white fiber, **C)** dried sample from wastewater treatment plant about to undergo FT-IR.

Hypothesis

- We predict greater microplastic abundance in organisms occupying higher trophic levels.
- The most common type of organismal polymer will be fibers.
- The most common type of plastic polymer would be polyester [PET].

Goal

- Polymeric characterization of microplastics found within the digestive tracts of aquatic organisms (at a later date wwtp samples).

Laboratory Methodology

- Organismal samples were obtained from Lake Champlain fishing tournaments and LCRI monitoring sampling events.
- Samples were processed using wet peroxide oxidation methods to remove biological material (Fig. 2).
- Samples were size separated in sieves: 1 mm (large), 355 µm (med), and 125 µm (small).
- Microplastics were characterized under the dissecting microscope according to type (e.g., fragment, fiber, foam, film, pellet/bead) (Fig. 3).
- Each characterized sample was placed in a Petri dish and dried in a drying oven at 55°C for 24hrs.
- Petri dishes were photographed as general reference and each microplastic particle was removed, individually photographed and placed on the FT-IR (Fig. 1C).
- Polymeric characterization occurred when the FT-IR spectrum for each microplastic particle was compared to known plastic and fiber libraries for a best polymeric spectrum match and search score (Figs. 1B, Figs. 4, 5).

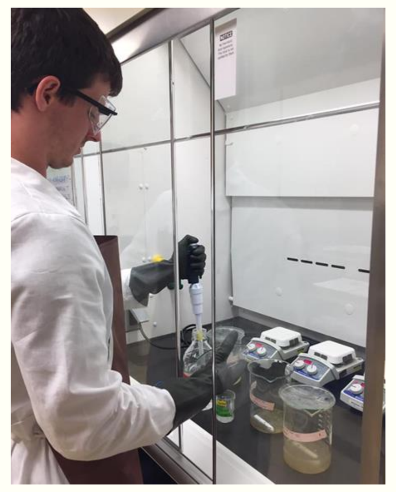


Fig. 2. Daniel Zobrowski performing wet peroxide oxidation.

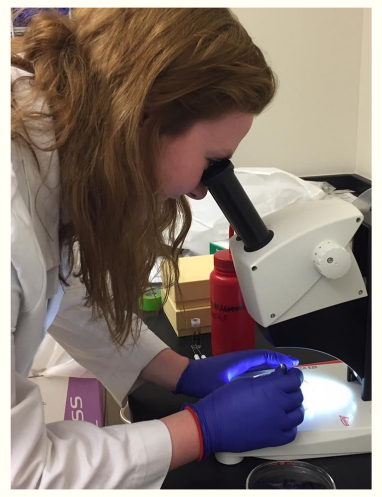


Fig. 3. Erin Ashline examining microplastics under the microscope.

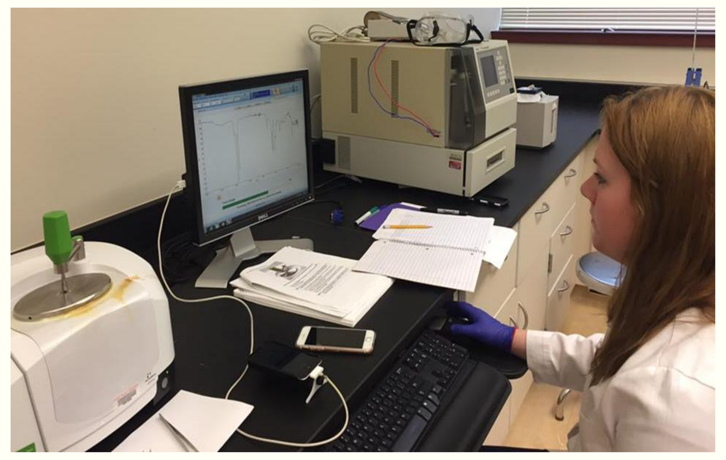


Fig. 4. Erin determining functional group peaks on an FT-IR spectrum (*Photo credit*: Vince Franke).

Fig. 5. Dr. Danielle Garneau and Erin Ashline examining "Best Polymeric Match" for a microplastic (*Photo credit*: Vince Franke).

Results

- **N = 20 species** from which microplastic particles were retrieved (Table 1).
- **N = 710 particles** were characterized **505 fibers** (polyester (PET); cellulose; rayon), **171 fragments** (polyester (PET); rayon; vinal; polypropylene), **14 pellets** (vinylidene chlorine; polyethylene chlorinated 36% chlorine; vinal; cellulose nitrate), **10 films** (rayon; poly [methylmethacrylate]; poly [1,4 cyclohexanedimethylene terephthalate], and **10 foams** (polyethylene, chlorosulfonated; polyethylene, chlorinated 36% chlorine; azlon (casein)).

Fig.6. Graphs of organismal Fibers, Fragments, Pellets/Beads, Films, and Foams.

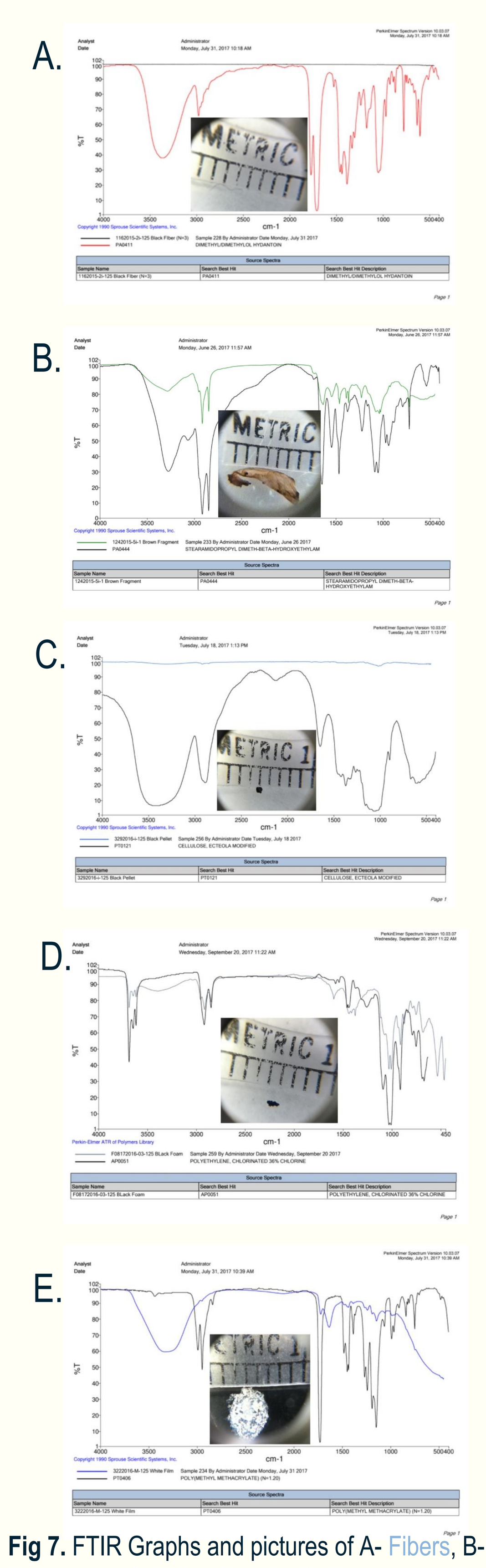


Fig 7 FTIR Graphs and pictures of A- Fibers, B- Fragments, C-Pellets/Beads, D- Foams, and E- Films

Results (cont.)

Table 1. Summary of organisms and dominant plastic polymer match.

Species	Total Particles	Total Fibers	Best Polymeric Match
Alewife	13	10	RAYON
Amphipod	2	2	NYLON
Arthropod	7	4	POLY(VINYL ALCOHOL) 88% HYDROLYZED
Atlantic salmon	3	3	RAYON
Bowfin	41	37	POLYESTER [PET]
Bullhead	3	3	ETHYLENE/VINYL ACETATE COPOLYMER 40% VINYL ACETATE
Double-crested cormorant	378	285	POLYESTER [PET]
Bluegull sunfish	3	2	AZLON [ALGINATE]
Lake trout	71	56	RAYON
Largemouth bass	33	30	RAYON
Mysids	3	2	RAYON
Northern pike	14	8	CELLULOSE(50U AVE PARTICLE SIZE)
Rainbow smelt	5	5	PROPYLENE GLYCOL MONOSTEARATE
Rock bass	11	11	POLYESTER [PET]
Slimy sculpin	2	2	CELLULOSE(20U AVE PARTICLE SIZE)
Sheepshead	3	3	PENTAERYTHRITOL MONORICINOLEATE
Smallmouth bass	94	24	POLYESTER [PET]
Rainbow smelt	27	18	RAYON
White perch	2	2	RAYON
Yellow perch	2	2	PROPYLENE GLYCOL MONOSTEARATE

Discussion

- Overall, polyester [PET] is the most common polymer and it derives from synthetic clothing and food and beverage packaging.
- PET is non-reactive and resistant to many chemicals and biological reactions, thus persists in the environment and has the potential to be mistaken for food by aquatic organisms.
- Polymers that ranked as most hazardous classified as mutagenic and/or carcinogenic which can negatively impact rates or reproduction and survival. These belong to the polymer families of polyurethanes, polyacrylonitriles, polyvinyl chloride, epoxy resins, and styrenic copolymers (Lithner et al. 2011).
- Textile fabric is intended for fabrication into functional articles of clothing, so as to increase functionality of the article of clothing, electronically conductive fibers are used. Fibers are generally found in most clothing. Incorporating electronically conductive materials increases functionality in textiles. But, this can lead to bioaccumulation (Textiles and textile products).
- Polyester [PET] has ability to absorb chemicals like methanol and toluene (Lune et al. 1997).

Potential Mitigation

- Modify consumer behavior to minimize plastic use in daily lives.
- When laundering clothing fiber emissions are quite high, especially with increasing population density (Browne et al. 2011, Hartline et al. 2016).
  → Front loading washing machine has less agitation, seek detergent alternatives (maybe), use products to capture fibers (Coraball-Rozalia Project, Guppybag-Patagonia).
- Reduce use of disposable/flushable baby wipes, which are largely comprised of fibrous plastics.
- Maintain marine/boating equipment (replace lines, nets etc.)

Future Directions

- Polymetric characterization of microplastics WWTP plant samples.
- Use inductively coupled plasma mass spectrometry (ICP-MS) to identify heavy metal and other chemical signatures on microplastics.

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References

Browne MA, Crump P, Niven SJ, Teuten E, Tonkin A, Galloway T, Thompson R. 2011. Accumulation of Microplastic on Shorelines Worldwide: Sources and Sinks. Environ. Sci. Technol. 45:9175-9179

Chakraborty, S., Bandyopadhyay, S., Ameta, R., Mukhopadhyay, R., & Deuri, A. (2007). Application of FTIR in characterization of acrylonitrile-butadiene rubber (nitrile rubber). Polymer Testing, 26(1), 38-41. doi:10.1016/j.polymertesting.2006.08.004

Lithner, D., Larsson, Å, & Dave, G. (2011). Environmental and health hazard ranking and assessment of plastic polymers based on chemical composition. *Science of The Total Environment, 409*(18), 3309-3324. doi:10.1016/j.scitotenv.2011.04.038

Fourier Transform Infrared Spectroscopy (FTIR) Analysis. (n.d.). Retrieved November 26, 2017, from http://www.intertek.com/analysis/ftir/

Hammer, C., and VanBrocklin, H. 2016. Microplastic Bioaccumulation in invertebrates, fish, and cormorants in Lake Champlain.

Hartline, N. L., Bruce, N. J., Karba, S. N., Ruff, E. O., Sonar, S. U., & Holden, P. A. (2016). Microfiber Masses Recovered from Conventional Machine Washing of New or Aged Garments. *Environmental Science & Technology, 50*(21), 11532-11538. doi:10.1021/acs.est.6b03045

Lune, F. S., Nijssen, L. M., & Linssen, J. P. (1997). Absorption of methanol and toluene by polyester-based bottles. *Packaging Technology and Science, 10*(4), 221-227. doi:10.1002/(sici)1099-1522(199707)10:4<221::aid-pts408>3.0.co;2-5

Lusher, A. L., Tirelli, V., O'Connor, I., & Officer, R. (2015). Microplastics in Arctic polar waters: the first reported values of particles in surface and sub-surface samples. Scientific Reports, 5, 14947. doi:10.1038/srep14947

Tagg, S., Sapp, M.,Harrison, J., Ojeda, J. 2015. Identification and Quantification of micro-plastics in wastewater using Focal Plane Array-based reflectance Micro-FT-IR imaging. *Analytical Chemistry* 87(12): 6032-6035

Textiles and textile products. Electrically conductive textiles. Determination of the linear electrical resistance of conductive tracks. (n.d.). doi:10.3403/30293513u

Vinodhini, R., & Narayanan, M. (2008). Bioaccumulation of heavy metals in organs of fresh water fish Cyprinus carpio (Common carp). International Journal of Environmental Science & Technology, 5(2), 179-182. doi:10.1007/bf03326011

Raphael A. Lavoie, Timothy D. Jardine, Matthew M. Chumchal, Karen A. Kidd, and Linda M. Campbell (2013) Biomagnification of Mercury in Aquatic Food Webs: A Worldwide Meta-Analysis. *Environmental Science & Technology* **2013** *47* (23), 13385-13394, DOI: 10.1021/es403103t