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. 2018), 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.
- 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 photodendrographic analysis 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 between plastics/fiber libraries for polymeric verification.
- FT-IR has been successful as 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 specifically rayon, polyester, and polystyrene polymers.
- 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 the environment as they bioaccumulate in tissues. Bioaccumulation in tissues reported similar results (Veselina and Narayan 2008). Ongoing SUNY Plattsburgh research on double-cast composites. 14 species of fish, and several invertebrate species confirms that microplastics are biomagnifying up the Lake Champlain food chain.

Results (cont.)
- N = 20 species from which microplastic particles were retrieved (Table 1).
- N = 716 particles were characterized 505 fibers (polyester [PET], cellulose, rayon), 171 fragments (polyester [PET], rayon, vinal, polycrylpropylene), 14 pellets (vinylidene chloride; polyethylene chlorinated 36% chlorine; vinyl; cellulose nitrate), 10 films (rayon; poly [methylene methacrylate]; poly [1,4 cyclohexanediymethylene terephthalate]), and 10 foams (polyethylene, chlorosulfonated; polyethylene, chlorinated 36% chlorine; vinal; cellulose nitrate).

Organisms
- Organisms 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).
- FT-IR was used to determine functional group peaks on an FT-IR spectrum (Fig. 3).
- 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).

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 retained for food by aquatic organisms.
- Polymers that ranked as most hazardous classified as mutagenic and/or carcinogenic which can negatively impact reproduction and survival. Those belong to the polymer families of polystyrenes, polycrylonitriles, polylcohyl chloride, epoxides, and styrene copolymers (Anther et al. 2011).
- Textile fabric intended for interaction into functional articles of clothing, so as to increase functionality of the article of clothing, electrically conductive fibers are used. Fibers are generally found in most clothing, incorporating electrically 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 (Brown et al. 2011, Hartline et al. 2016).
  - Front loading washing machine has less agitation, seek detergent alternatives (magnets), use products to capture fibers (Corbella-Rolaza Project, Guypayag/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
- Polymeric characterization of microplastics WWTP plant samples.
- Use conductively coupled plasma mass spectrometry (IC-MS) to identify heavy metal and other chemical signatures on microplastics.

Acknowledgments
Special thanks to Dr. Sheri Mason (SUNY Fredonia) for guidance and inspiration in this microplastic research. Special thanks to the Lake Champlain Research Institute (LCRI) for use of their microscopes and equipment, as well as fishers and members of Lake Champlain International (Slie Hager) who contributed fish specimens. Thanks to Luke Meyers for invertebrate samples. Funding was provided by a NOAA funded Lake Champlain Sea Grant. Lastly, thank you to all the technical support from Jeff Jones and Dr. Rash and to every student who was part of this research collaboration.

References

Table 1. Summary of microplastics found in Lake Champlain

<table>
<thead>
<tr>
<th>Species</th>
<th>Total Polymers</th>
<th>Total Fibers</th>
<th>Best Polymeric Match</th>
</tr>
</thead>
<tbody>
<tr>
<td>Species A</td>
<td>12</td>
<td>15</td>
<td>Polyester [PET]</td>
</tr>
<tr>
<td>Species B</td>
<td>13</td>
<td>16</td>
<td>Polyethylene</td>
</tr>
<tr>
<td>Species C</td>
<td>14</td>
<td>17</td>
<td>Polyvinylidene chloride</td>
</tr>
<tr>
<td>Species D</td>
<td>15</td>
<td>18</td>
<td>Polyethylene terephthalate</td>
</tr>
</tbody>
</table>

Fig. 1. A) Polyester fiber 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 going SUNY Plattsburgh.

Fig. 2. Samples were processed using wet peroxide oxidation methods to remove biological material (Fig. 2).

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

Fig. 4. Erin Ashline examining microplastics under the microscope.

Fig. 5. Dr. Danielle Garneau and Erin Ashline examining “Best Polymeric Match” for a microplastic (Photo credit: Vinci Franke).

Fig. 6. Graphs of organismal fibers, fragments, pellets/beads, films, and foams.