Fate of textile microfibers released during home laundering in aquatic environments: the effect of fabric type, washing conditions, and finishes

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“Microplastics are any synthetic solid particle or polymeric matrix, with regular or irregular shape and with size ranging from 1 \( \mu m \) to 5 mm, of either primary or secondary manufacturing origin, which are insoluble in water”.

Frias and Nash (2019)

Main Sources of Primary Microplastics in Aquatic Environments

Primary MPs enter the oceans in the form of small particles.

One of the main sources of primary MPs are micro-size fibers or “MICROFIBERS” released from textiles during laundering.

Only in US and Canada, \textbf{878 tons or 3.5 quadrillion microfibers per year} make it to environment via WWTP (wastewater treatment plants), equivalent to \textbf{89 million plastic bottles}.

Boucher and Friot (2017) and Ocean Wise (2019)
Background

Microplastics Distribution

Microplastics are EVERYWHERE!!!

The average person ingests over 5,800 particles annually of synthetic debris from beer (4 particles/L), tap water (5 particles/L), and sea salt (212 particles/kg).

Kosuth et al. (2018)

The presence of anthropogenic debris in seafood for human consumption has been observed.

Miranda and de Carvalho-Souza (2016) and Rochman et al. (2015)

Human stool samples have shown between 18 to 172 plastic particles per 10 g of stool.

Schwabl (2018)

www.adventurescientists.org/microplastics.html
Kosuth et al. (2018), Miranda and de Carvalho-Souza (2016), and Rochman et al. (2015)
Background

Impacts of Microplastics on the Environment

Rummel et al. (2017)

Mishra et al. (2019)
How do Textile Microfibers Go to the Environment?

Objectives

Study the fate and role of textile natural fibers in the anthropogenic pollution of freshwater and marine environments

Research Questions

1. Do cotton fabrics release more particles/fibers than synthetic fabrics during laundering?

2. Are these textile fibers biodegradable in aquatic environments?

3. Do the textile finishes applied to cotton for better performance impact their fate in aquatic environments?
Research Questions

Do cotton fabrics release more particles/fibers than synthetic fabrics during laundering?

Parameter Studied:
- Fabric type (100% cotton, 100% polyester, 50/50 polyester/cotton, and 100% rayon)
- Accelerated laundering (lab scale) vs Home laundering
- Washing parameters
- Effect of fiber chemical structure and morphology
- Influence of mechanical properties of fabrics and yarns.

Experimental Plan

Accelerated Laundering (lab scale)  
SDL Atlas Laundrometer

Synthetic vs Cellulose-Based Fabrics  
Knitted (Interlock) Fabrics  
- 100% Rayon  
- 100% Cotton  
- 50/50 Polyester/Cotton  
- 100% Polyester

Home Laundering  
Washing Machine  
45 gallons

Parameters Studied:  
Type of Fabric.  
Subsequent washing and drying cycles

Quantification  
Fibers Quality Analyzer  
HiRes FQA  
Filtration and Weighing

Parameters Studied:  
Type of Fabric.  
Washing with liquid detergent vs water.  
Temperature (25 °C vs 44 °C)  
4 in x 4 in (0.006 Lb.)  
4 Lb.
Synthetic vs Natural Fabrics

The microfibers released during home laundering in the US per year estimated at 3000 tons.

Accelerated Laundering

Home Laundering
Results

Accelerated laundering vs Home laundering

Mass of microfibers released during home laundering (N=1) and accelerated laundering (T= 44 °C, with detergent N=4) per mass of fabric washed.

Error bars represent the standard error.

Mean values are shown for all the variables.
Results

Washing Parameters

**EFFECT OF DETERGENT**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>With detergent (WD)</th>
<th>Without detergent (WOD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>44 °C</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>Polyester</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyester/Cotton</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rayon</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cotton</td>
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**EFFECT OF TEMPERATURE**

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Significant differences are indicated by * (p<0.05)
Results

Microfibers size distribution

- Microfibers shed from laundering detected in our experiments → 200 µm - 2 mm.
- Fibers used to spin yarns → > 25 mm.
- This indicates that the textile fibers are broken during washing.
- Small size: easy to ingest……hard to detect.
Summary

- All fabric types tested shed microfibers, however, cellulosic fabrics released more microfibers than synthetic fabrics in both the accelerated and home laundering experiments.

- In the accelerated laundering experiments, more microfibers were generated per mass of fabric washed than in the home laundering experiments as a result of the more intense mechanical action of the metal balls.

- The generation of microfibers from laundering is most affected by the use of detergent as washing agent, nevertheless, temperature also tends to increase the amount of microfibers released.

- The accelerated laundering experiment has several advantages over home laundering for studying microfibers generation and is considered to be an insightful indication of fabric shedding.
Research Questions

Are these textile fibers biodegradable in aquatic environments?

Parameter Studied:

- Yarn/fiber type (100% cotton, 100% polyester, 50/50 polyester/cotton, and 100% rayon)
- Aerobic biodegradability of textile yarns
- Freshwater and marine environments
- Effect of fiber chemical structure and morphology
- Interactions with the local microbiome

Experimental Plan

Samples:
- Blank
- 100% Cotton
- 100% Polyester
- 100% Rayon
- 50%/50% Polyester/Cotton
- Reference Microcrystalline Cellulose

Inoculum:
- Lake Water
  - Lake Raleigh, NC
  - ISO 14851
- Seawater
  - Wilmington, NC
  - ASTM D6691
- Activated Sludge
  - Neuse River WWTP, NC
  - ISO 14851

Biodegradation Measurements
Respirometer System
- RSA PF-8000

\[
\% \text{ Biodegradation} = \frac{O_u}{\text{ThOD}} \times 100
\]

- \(O_u\) - Oxygen Uptake
- \(\text{ThOD}\) - Theoretical Oxygen Demand
Experimental Plan

Inoculum → Biodegradation Under Lab-Controlled Conditions → Characterization

O₂ → DNA Extraction → NGS → Data Analysis

CO₂ → Aqueous Test Medium

Spun Yarns Length 5mm → Solid Remaining → SEM → FTIR → Data Analysis

**SEM** Scanning Electron Microscopy, **FTIR** Fourier-Transform Infrared Spectroscopy, **NGS** Next Generation Sequencing
Results

Aerobic Biodegradation of Textile Spun Yarns

<table>
<thead>
<tr>
<th>Samples</th>
<th>Lake Water N=360</th>
<th>Seawater N=320</th>
<th>Activated Sludge N=556</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCC (Reference Material)</td>
<td>81.06 ± 0.24</td>
<td>71.02 ± 0.49</td>
<td>105.42 ± 0.4</td>
</tr>
<tr>
<td>100% Cotton Spun Yarns</td>
<td>77.22 ± 0.41</td>
<td>48.50 ± 0.21</td>
<td>89.12 ± 0.48</td>
</tr>
<tr>
<td>100% Rayon Spun Yarns</td>
<td>72.71 ± 0.20</td>
<td>45.87 ± 1.20</td>
<td>87.01 ± 0.58</td>
</tr>
<tr>
<td>50/50 Polyester/Cotton Spun Yarns</td>
<td>32.84 ± 0.36</td>
<td>14.40 ± 0.48</td>
<td>45.22 ± 0.33</td>
</tr>
<tr>
<td>100% Polyester Spun Yarns</td>
<td>No Appreciable</td>
<td>4.24 ± 0.42</td>
<td>5.22 ± 0.15</td>
</tr>
</tbody>
</table>

Biodegradation curves of the textile yarns based on the oxygen uptake of the system versus the theoretical oxygen demand calculated for each yarn, corrected for nitrification reactions.

A – Inoculum: Lake Water from Lake Raleigh (Raleigh, NC), method ISO 14851 (N=3). B – Inoculum: Seawater from Fort Fisher Park (Wilmington, NC), method ASTM D6691 (N=4). C – Inoculum: Activated sludge from the Neuse River WWTP, 30 ppm of total suspended solids (TSS), method ISO 14851 (N=4). The error bars represent the standard error of the mean.
Results

Aerobic Biodegradation of Textile Spun Yarns

Textile spun yarns before biodegradation (left, initial) and residual solids after biodegradation (right, final)

Biodegradation in aquatic media using as inoculum 30 ppm of total suspended solids (TSS) of activated sludge from the Neuse River WWTP.
Microbiome Analysis

Sample Collection → Isolate/Purify Genomic DNA → Amplify DNA from 16S rRNA regions and barcode samples with Illumina indexes → Next Generation Sequencing → Data Analysis

- Bacteria
- Illumina MiSeq 300 PE
- MultiQC
- NEPHELE
- DADA2
- Phyloseq
- DeSeq2
- Origin
Results

Bacterial diversity analysis

Order abundance from the 16S rRNA marker gene survey in the biodegradation of textile yarns in lake water

Based on Top 20 Most abundant Amplicon Sequence Variants (ASV).

Principal coordinate analysis (PCoA) from the 16S rRNA marker gene survey in the biodegradation of textile yarns in lake water

The biodegradable samples (MCC, cotton, and rayon) are clustered inside a green circle with dashed lines, the non-degraded samples (polyester and blank) are clustered inside a red circle with dotted lines, and the initial lake water replicates are clustered inside a black circle with solid lines. Colors and shapes of the data points denote the different replicates of the samples.
Summary

- Cellulose-based fibers biodegrade quickly both in aquatic and marine environments and synthetics do not.
- The biodegradation potential with the different inoculums is the same: MCC > Cotton > Rayon > Polyester/Cotton >> Polyester
- Biodegradation depends on ALL of the following:
  ✓ Yarn material.
  ✓ Abiotic characteristics of the water.
  ✓ Microorganisms present in the environment.
- There are distinct microbial communities developed during the biodegradation process according to the material inoculated.
- Distinct bacterial genus related to the assimilation of complex carbohydrates were identified in the test media containing cellulosic materials as source of carbon.
- Bacterial communities existing in the polyester sample after the experiments were very similar to that of the blank sample, confirming the incompatible nature of the polyester and the bacterial communities.
Research Questions

Do the textile finishes applied to cotton for better performance impact their fate in aquatic environments?

Parameter Studied:

- Fabrics with different finishing treatments (dye, durable press, softener, and water repellent)
- Aerobic biodegradability of cotton microfibers
- Kinetic models for biodegradation
- Interactions with *cellulases*
- Surface and bulk properties related with biodegradation

Experimental Plan

**Enzymatic Hydrolysis**

**Conditions:**
- 200 mg of Fabric
- 2 ml of Enzyme/L
- 10 ml 0.1 M Acetate Buffer (pH 5)
- Incubation at 50 °C for 3 Days
- Glucose release measured by HPLC

**Enzyme Adsorption**

- Uberbacher et al. (2009)

**Fabrics + Enzyme**

Celluclast® 1.5L (Novozymes), Cellulase from *Trichoderma reesi*

1,4-(1,3:1,4)-β-D-Glucan 4-glucanohydrolase

Enzyme Activity 700 EGU/g

EGU – Amount of Enzyme releasing 1µmol/min at 50 °C and pH 4.8

**Enzyme Adsorption Conditions:**
- 20 mg of Fabric
- 245 µg of Enzyme/mL
- 600 µL 0.1 M Acetate Buffer (pH 5)
- Incubation at 4 °C for 4 hours
- Protein Concentration measured by the Pierce™ Rapid Gold BCA Protein Assay Kit
Results

Effect of finishes on cotton biodegradation in aquatic environments

Samples | % Biodegradation
---|---
Cotton – Softener | 89.6 ± 10.9 %
Reference Material (MCC) | 87.7 ± 5.4 %
Cotton – Water Repellent | 74.9 ± 0.7 %
Cotton – No Finish | 72.2 ± 7.0 %
Cotton – Dye | 66.2 ± 9.8 %
Plant Material (Oak Leaves) | 64.9 ± 2.3 %
Cotton – Durable Press | 63.0 ± 1.0 %

Effect of finishes on the biodegradation of the cotton microfibers

Softener > MCC > Water Repellent ~ No Finish > Dyed ~ Oak Leaves > Durable Press

No Significant Difference (α=0.05)

Biodegradation curves based on the standard method ISO 14851:1999 for the determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium (ISO 14851:1999, 2005). As inoculum 30 ppm TSS of activated sludge from Neuse River WWTP was used. The percentage of biodegradation was based on the oxygen uptake of the system versus the theoretical oxygen demand calculated for each yarn. The error bars represent the standard error of the mean (N=3), for oak leaves N=2.
Results

Kinetic models for biodegradation

Gompertz Model

\[ M = P \times \exp \left\{ -\exp \left[ \frac{R \times e}{P} (\lambda - t) + 1 \right] \right\} \]

<table>
<thead>
<tr>
<th>Treatment</th>
<th>( P ) (mg O(_2)/g initial material)</th>
<th>( R ) (mg O(_2)/g initial material*day)</th>
<th>( \lambda ) (days)</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Finish</td>
<td>836.2 ± 10.2</td>
<td>81.0 ± 11.7</td>
<td>3.5 ± 0.8</td>
<td>0.86</td>
</tr>
<tr>
<td>Dye</td>
<td>775.2 ± 15.6</td>
<td>77.4 ± 18.7</td>
<td>4.3 ± 1.3</td>
<td>0.70</td>
</tr>
<tr>
<td>Durable Press</td>
<td>740.0 ± 8.8</td>
<td>16.2 ± 0.7</td>
<td>5.9 ± 0.9</td>
<td>0.97</td>
</tr>
<tr>
<td>Softener</td>
<td>993.9 ± 18.3</td>
<td>55.1 ± 8.5</td>
<td>2.3 ± 1.5</td>
<td>0.77</td>
</tr>
<tr>
<td>Water Repellent</td>
<td>869.4 ± 4.9</td>
<td>56.7 ± 2.9</td>
<td>7.7 ± 0.4</td>
<td>0.98</td>
</tr>
</tbody>
</table>

M = cumulative oxygen consumption (mg O\(_2\)/g initial material)

P = Ultimate oxygen consumption (mg O\(_2\)/g initial material)

R = Oxygen Consumption Rate (mg O\(_2\)/g initial material*day)

\( \lambda \) = lag-phase period (days)

t = time (days)

e \approx 2.718282

Rate (R) \( \rightarrow \) No Finish > Dye > Water Repellent > Softener >> Durable Press

Lag-Phase (\( \lambda \)) \( \rightarrow \) Softener < No Finish < Dye < Durable Press < Water Repellent
Results

SEM images of the fibers during aerobic biodegradation
Results

Interactions with cellulases

Effect of Finishes on Cotton Enzymatic Hydrolysis by Cellulase

Effect of Finishes on Adsorption of Cellulase on Cotton Fabrics
Results

Surface properties of finished fabrics

Distribution of Finishes of the Surface of the Fabric (before biodegradation) by ToF SIMS (Negative Ions)

Red - Cellulose
Green - Finishes

No Finish

72% Biodegradation

Red – CH₂O₂; C₆H₄O₂; C₆H₅O₂; C₆H₇O₂
Green – CN

66% Biodegradation

Dye

Red – CH₂O₂; C₆H₄O₂; C₆H₅O₂; C₆H₇O₂
Green – SO₃

63% Biodegradation

Durable Press

Red – CH₂O₂; C₆H₄O₂; C₆H₅O₂; C₆H₇O₂
Green – CNO; CN

75% Biodegradation

Water Repellent

Red – CH₂O₂; C₆H₄O₂; C₆H₅O₂; C₆H₇O₂
Green – SiC₆H₄O₂; SiC₆H₄H₂O₂

90% Biodegradation

Softener
Summary

- The finishes applied during textile processing on cotton fabrics affect their biodegradation in aquatic environments.
- In general, the biodegradation of fabrics with some levels of crosslinking in the finishing treatment were more affected:
  - The cotton fabric with water repellent finish has the longest lag-phase ($\lambda$).
  - Cotton fabrics with durable press finish degraded the least among the samples and had the lowest degradation rate ($R$).
- The finishes applied during textile processing on cotton fabrics affect their ability to be hydrolyzed by Cellulase.
  - Glucose released: No Finish > Softener > Dye >> Water Repellent ~ Durable Press
- The finishes applied during textile processing on cotton fabrics affect the binding ability of Cellulase to the surface of the fabric:
  - No Finish ~ Dye ~ Softener >> Durable Press ~ Water Repellent
- Similarly to the biodegradation results, the fabrics that have crosslinking (durable press and water repellent) and high hydrophobicity (water repellent) on the surface delay the penetration of enzymes within the polymeric matrix. The crosslinking on the surface reduce the availability of binding sites on the cotton structure.
Concluding Remarks

- The textile industry is a contributor to the microfiber issue.

- All fiber types tested shed microfibers, however, synthetic fibers are more persistent in the environment.

- Cellulose-based fibers biodegrade quickly both in aerobic simulated and natural aquatic environments and synthetics do not.

- Cellulose-based and synthetic polymer-based microfibers promote DIFFERENT changes in the microbiome.

- The finishes applied to textiles for performance influence the rate of biodegradation.

- Fiber persistence and quantity should be considered in test methods and decisions regarding sustainability in the textile industry.
Acknowledgments

Thank you!
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