Are Microplastics a Vector for Chemical Contaminants?

A.D. Steinman, M.E. Oudsema, and R.R. Rediske – Annis Water Resources Institute, Grand Valley State University

L. Green, J.W. Scott, and N. Holm – Illinois Sustainable Technology Center, University of Illinois

Grand Valley State University
Robert B. Annis Water Resources Institute

ILLINOIS
Illinois Sustainable Technology Center
PRAIRIE RESEARCH INSTITUTE

Today's Presentation

- Overview of Microplastics Issue
- Microplastic Survey in Muskegon Lake
- Experimental Results for Persistent Organic Pollutants (POPs) adsorption by microplastics in Muskegon Lake

What are microplastics?

- Plastics that are less than 5 mm in length

Where do microplastics come from?

- Estimated that 8.3 billion metric tons of plastic produced to date.

- 79% of this material deposited in landfills and the natural environment.

- Primary sources of microplastics (e.g., nurdles, additives to consumer products)

- Secondary sources of microplastics as a result from breakdown of larger plastic materials.

Where are we finding microplastics ?

- Air and dust
- Food and beverages
- Cosmetics
- Wastewater
- Industrial wastewater
- Surface water
- Sediments and soil
- Wildlife
- Karst groundwater

- And everywhere else we look

Are humans exposed to microplastics?

- Humans consume over 100 microplastic particles/day and can inhale up to 170/day.
- Bottled water increases microplastic consumption 2 to 3x that of tap water.
- A great deal of variation in reported microplastic data → attributed to lack of standard methods of analysis.
- Need to develop standardized methods for analysis of microplastics.

Source: Cox et al. 2019. Environmental Science & Technology.

Are there adverse health effects from exposure to microplastics?

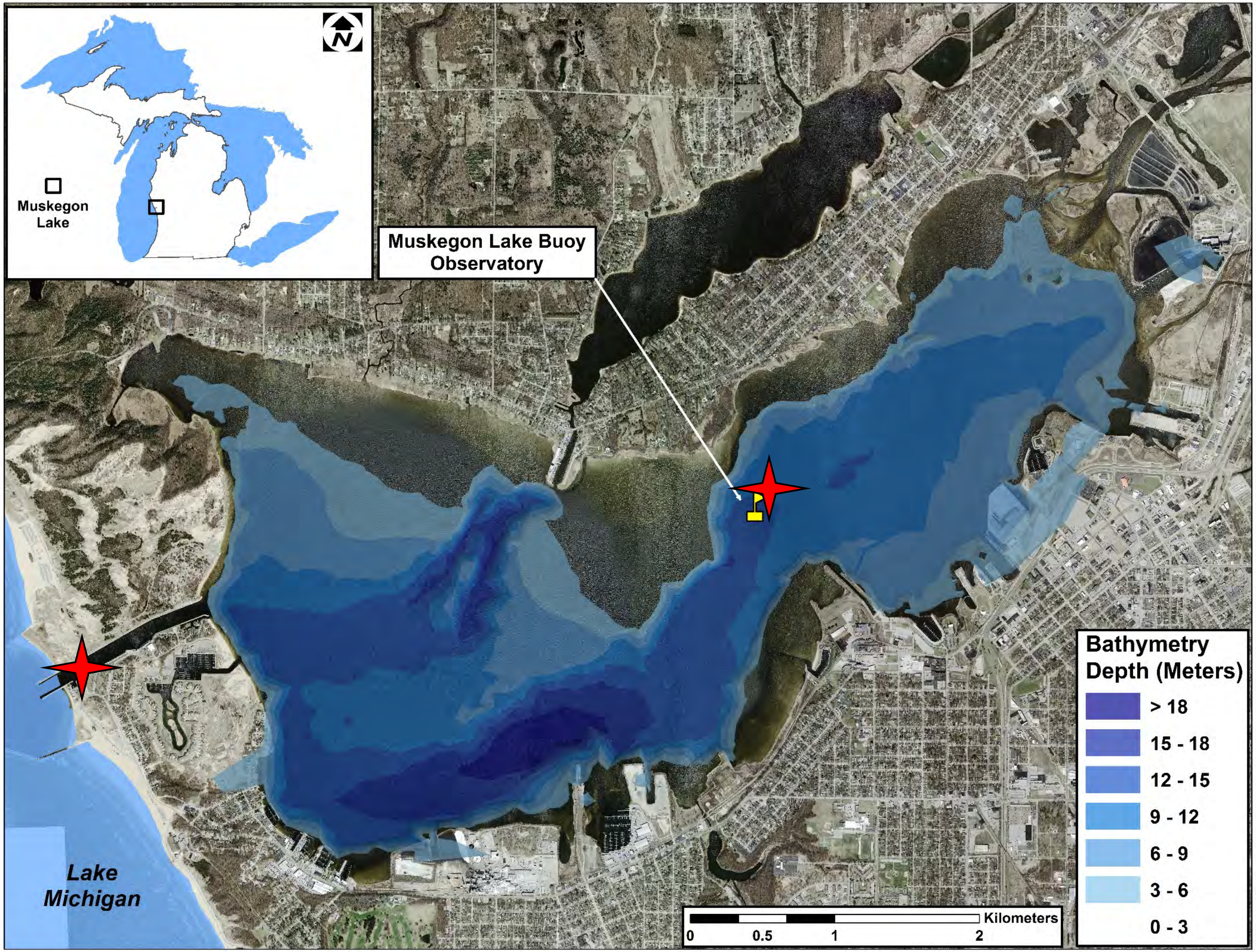
Source: journals.openedition.org

- Adverse effects on wildlife currently under investigation. Some studies show neutral effects, others show negative effects.
- Adverse effects on humans are largely unknown.
- Exposure to heavy metals and additives used in plastic materials.
- Microplastics can concentrate legacy and emerging contaminants from the environment.
- Vectors for pathogens and viruses.

Source: Foley et al. 2018. *Science of the Total Environment* 631 (2018): 550-559.

Microplastics in Muskegon Lake (water column)

- Type of Microplastic
- Color



Muskegon Lake
Muskegon Lake Buoy Observatory
Bathymetry Depth (Meters)
> 18
15 - 18
12 - 15
9 - 12
6 - 9
3 - 6
0 - 3
Kilometers
0
0.5
1
2
Lake Michigan
N

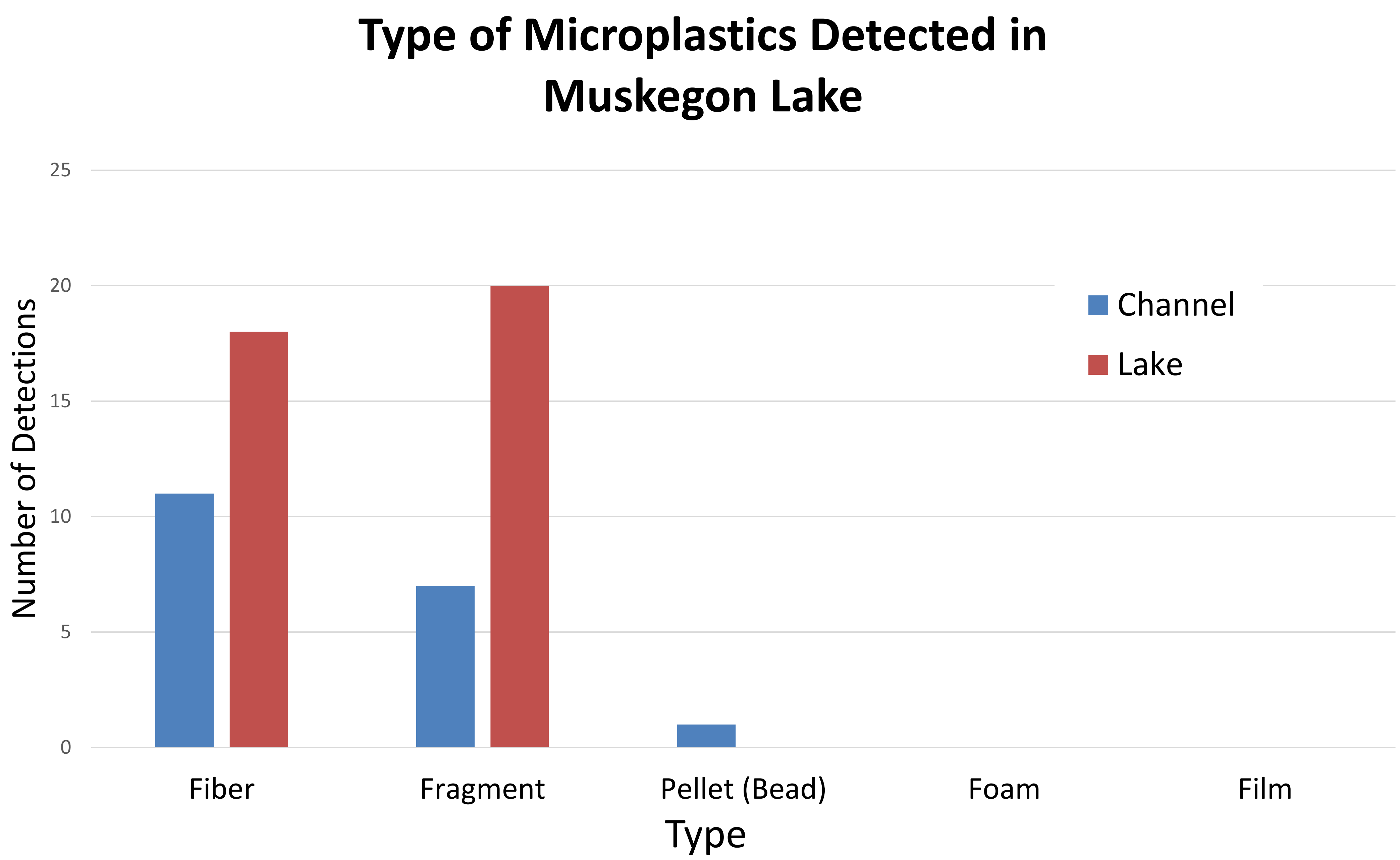
Methods – Microplastic Survey

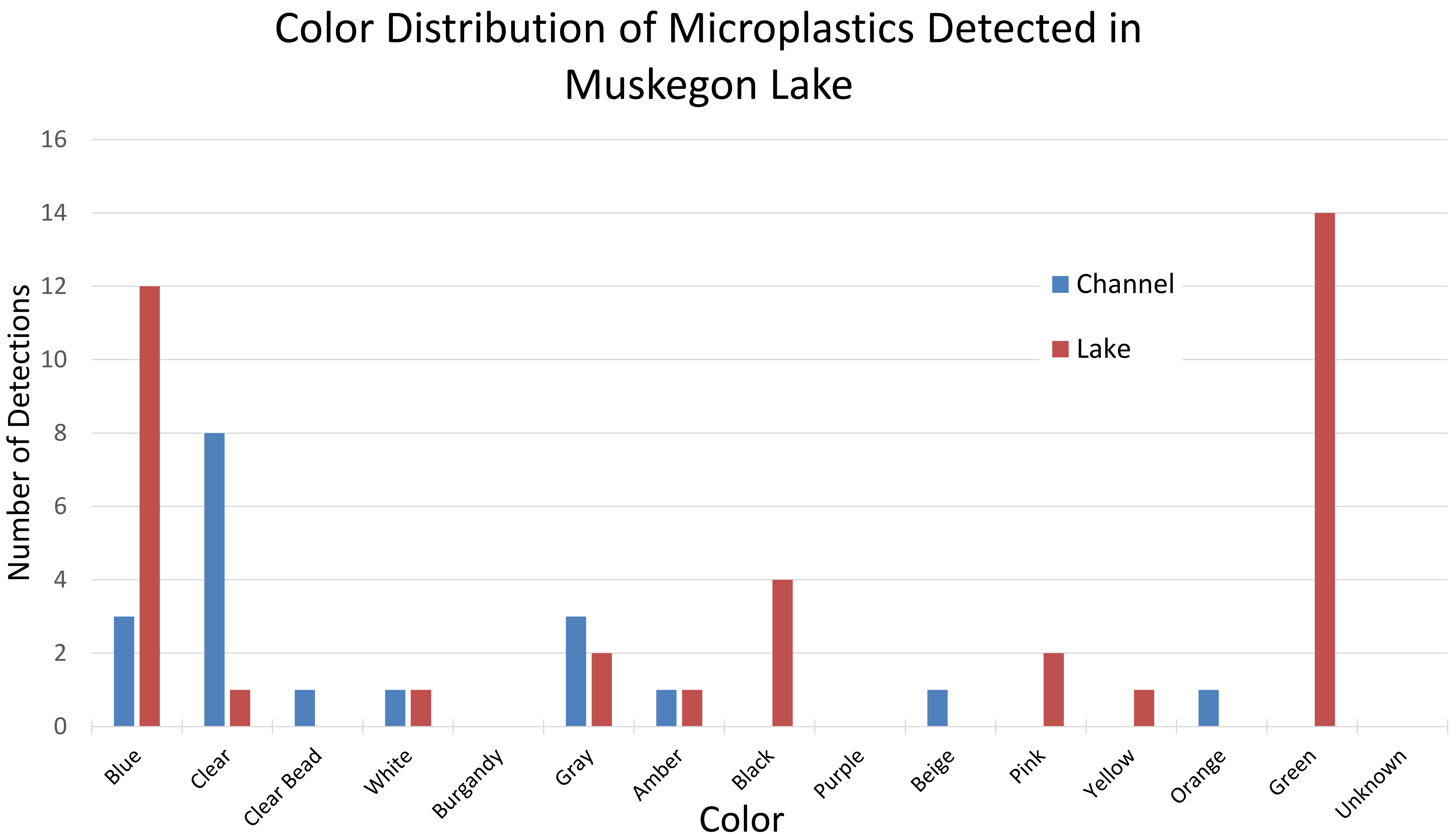
- Grab Samples (Cleaned/Fired Glass Jars)
- 2 sites: channel and buoy
- Modified NOAA protocol
  - Sieving (5 µm), organic digestion, density separation (<1.8 g/L), and isolation on 0.45µm filter
- Microscopic analysis (Counting and Sizing)
  - Zeiss SteREO Discovery V20 Microscope
  - Size limit of detection 5 µm

Methods – Microplastic Survey Results

Microplastic Densities:

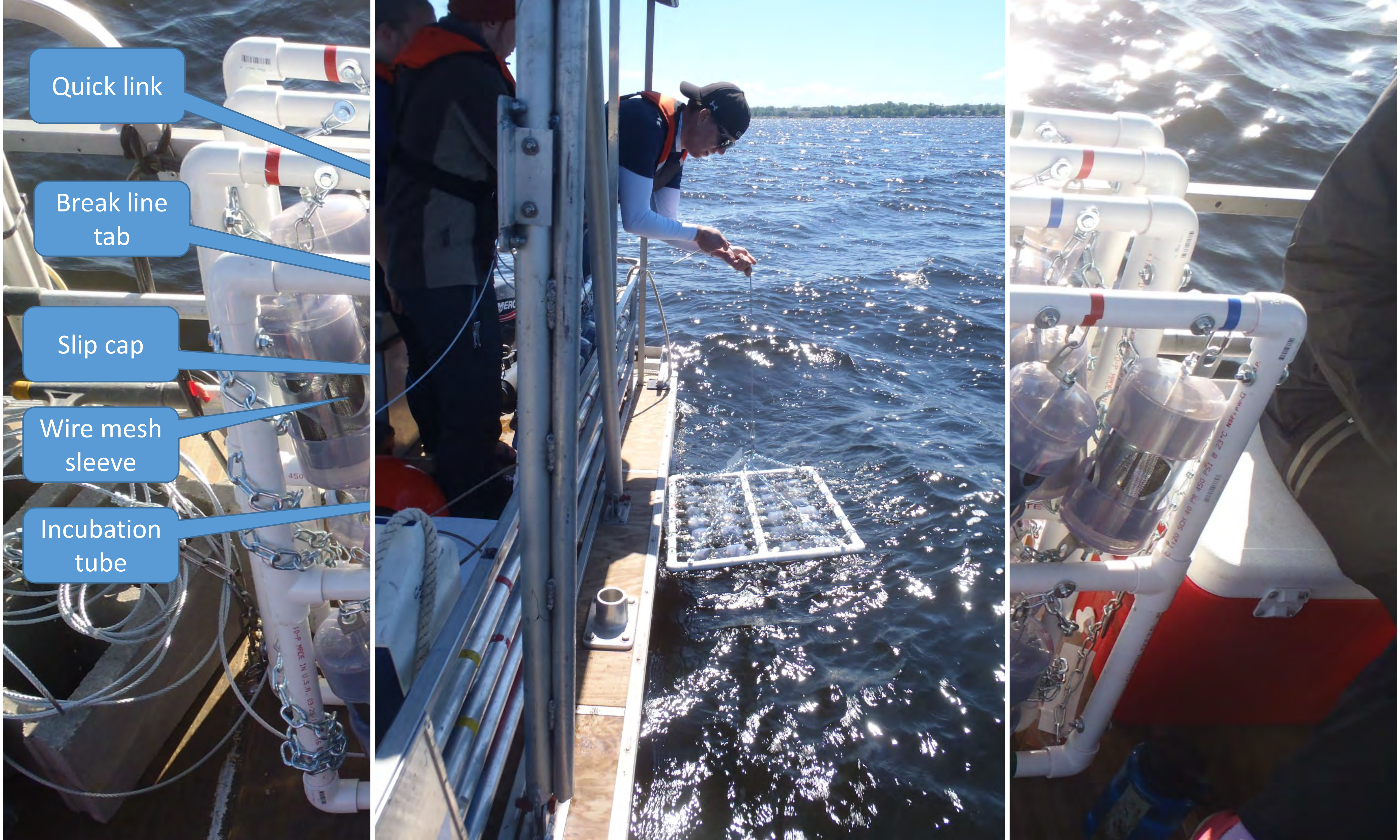
- Lake open water: 31 particles/L
- Channel: 12 particles/L

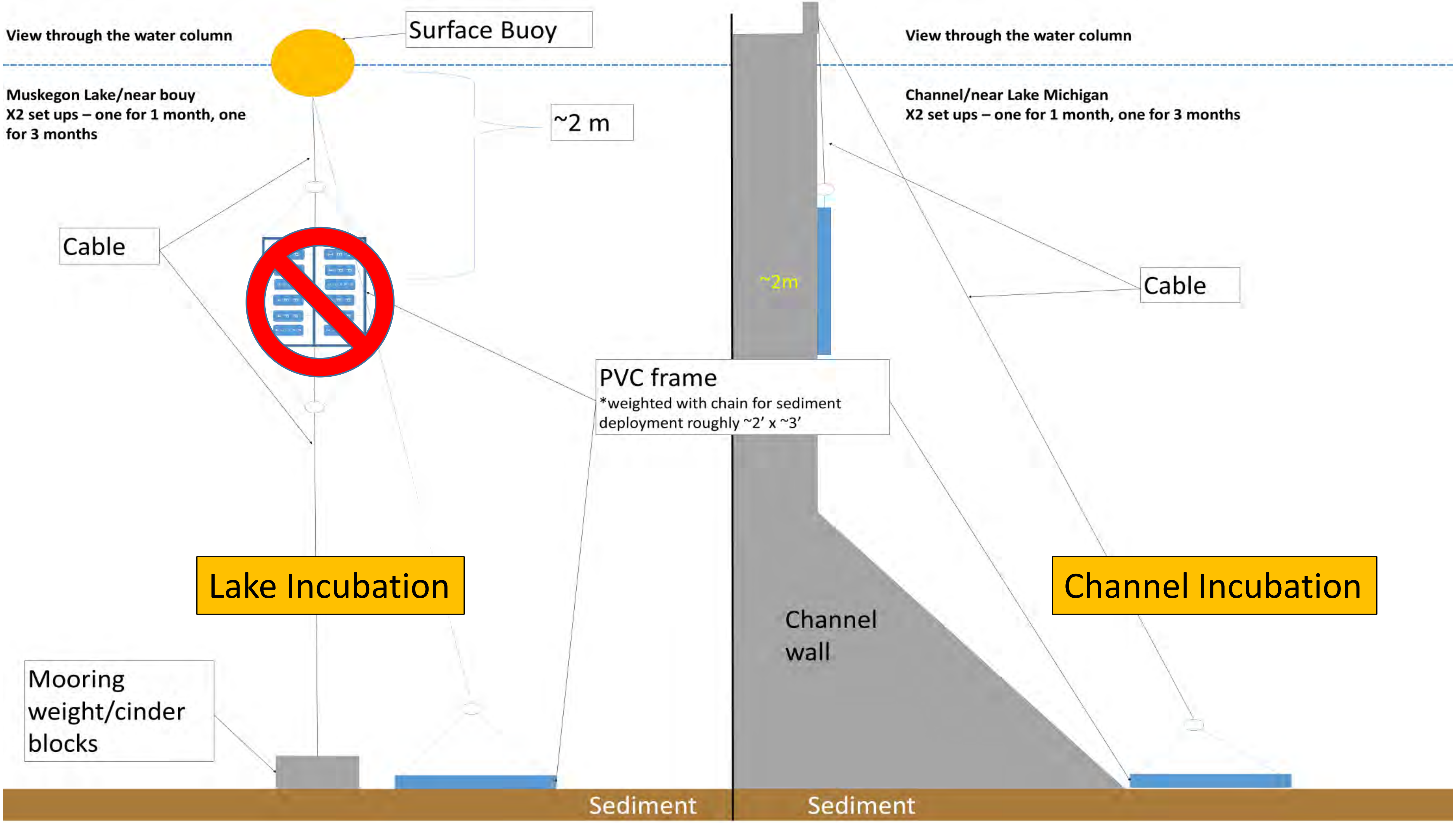

Type of Microplastics Detected in Muskegon Lake
Number of Detections
25
20
15
10
5
0
Channel
Lake
Fiber
Fragment
Pellet (Bead)
Foam
Film
Type


Color Distribution of Microplastics Detected in Muskegon Lake
Number of Detections
0
2
4
6
8
10
12
14
16
Channel
Lake
Blue
Clear
Clear Bead
White
Burgandy
Gray
Amber
Black
Purple
Beige
Pink
Yellow
Orange
Green
Unknown
Color

Experimental Deployment of Microplastics in Muskegon Lake

- Deploy 3 types of Microplastics (polyester; polypropylene; polyethylene)
- 2 sites; 2 depths
- Collect water (Van Dorn bottles) and sediment samples at time of deployment
- Retrieve after 1 and 3 months
- Analyze for variety of contaminants


Quick link
Break line tab
Slip cap
Wire mesh sleeve
Incubation tube


View through the water column
Surface Buoy
Muskegon Lake/near bouy
X2 set ups – one for 1 month, one for 3 months
~2 m
Cable
PVC frame
*weighted with chain for sediment deployment roughly ~2' x ~3'
Lake Incubation
Mooring weight/cinder blocks
Sediment
View through the water column
Channel/near Lake Michigan
X2 set ups – one for 1 month, one for 3 months
~2m
Cable
Channel wall
Channel Incubation
Sediment

Target Contaminants

- Polyaromatic Hydrocarbons (PAHs) – 16 Compounds
- Polychlorinated Biphenyls (PCBs) – 27 Congeners
- Chlorinated Pesticides (OCs) – 12 Compounds
- Polybrominated Biphenyl Ethers (PBDEs) – 9 Congeners
- Perfluoroalkyl substances (PFAS) – 7 Compounds
- Heavy Metals – Cr, Mn, Cu, Zn, As, Se, Ag, Cd, and Pb

Sample Preparation – Water Samples

Aqueous Samples (POPs)

- Liquid-Liquid extraction with dichloromethane
- Extract drying under sodium sulfate
- Silica gel fractionation
- Exchange to hexane and concentrate to 1.0 mL final volume

Sample Preparation – Plastic Samples

Plastics (POPs)

- Accelerated solvent extraction (ASE 300) with hexane
- Silica gel fractionation
- Exchange to hexane and concentrate to 1.0 mL final volume

Plastics (Metals)

- Microwave digest with nitric acid and dilute to final volume 50 mL in DI water

Associated Quality Control

Per Sample – 18 POP Surrogates and 11 POP internal standards

- Per Preparation Batch
- All samples prepared in triplicate
- Reagent blank & reagent blank spike
- Silica gel quality control spike
- Sample matrix spike
- Analytical sample duplicate
- Analytical spike sample

Sample Analysis

PAHs and PCBs

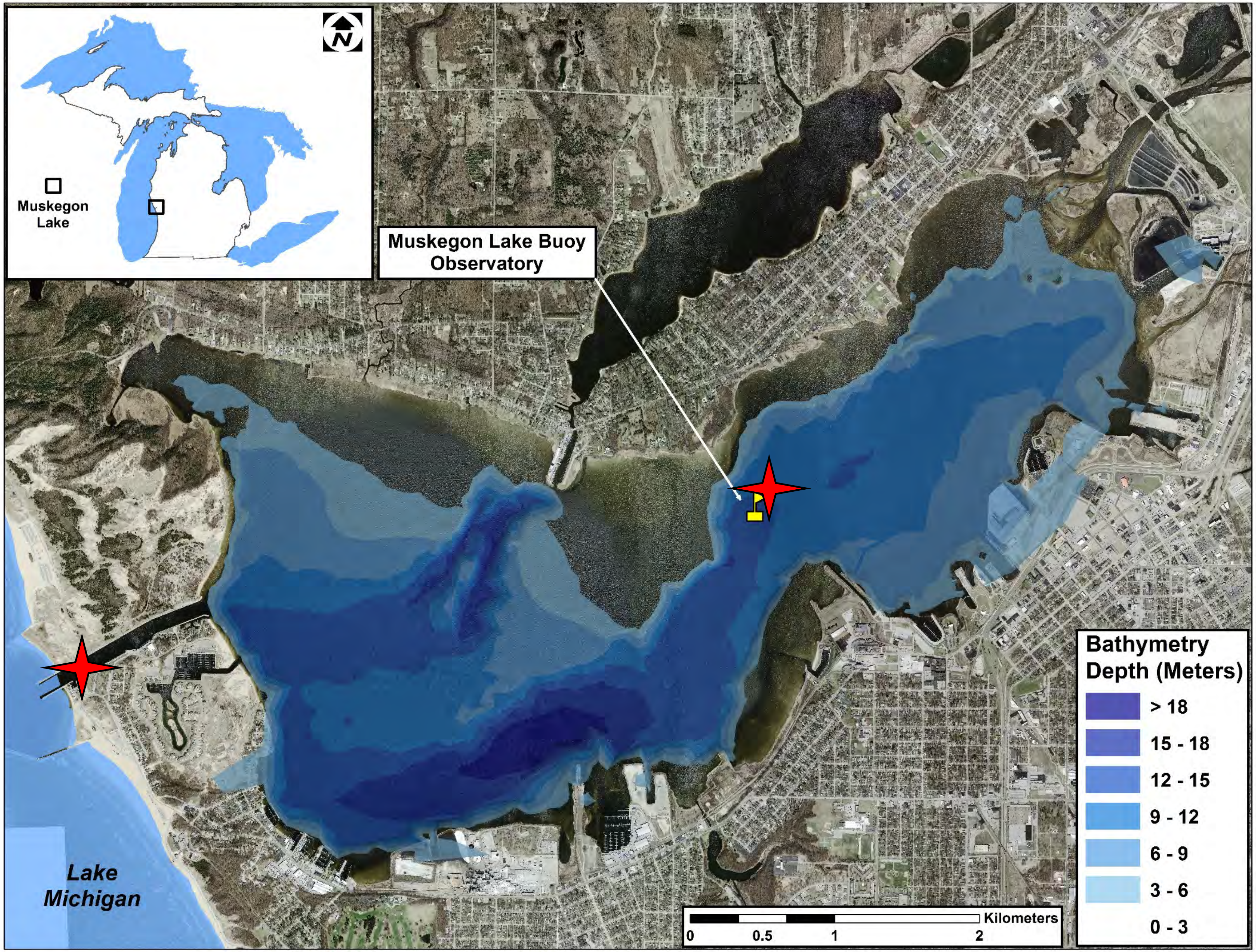
- Shimadzu QP-2010 SE Gas Chromatography Mass Spectrometer

DDT, DDE, DDD, OCs, and PBDEs

- Agilent 6890 Gas Chromatograph coupled to an Autospec Ultima High Resolution Mass Spectrometer

Metals

- VG PQ ExCell Inductively coupled plasma mass spectrometer


Muskegon Lake
Muskegon Lake Buoy Observatory
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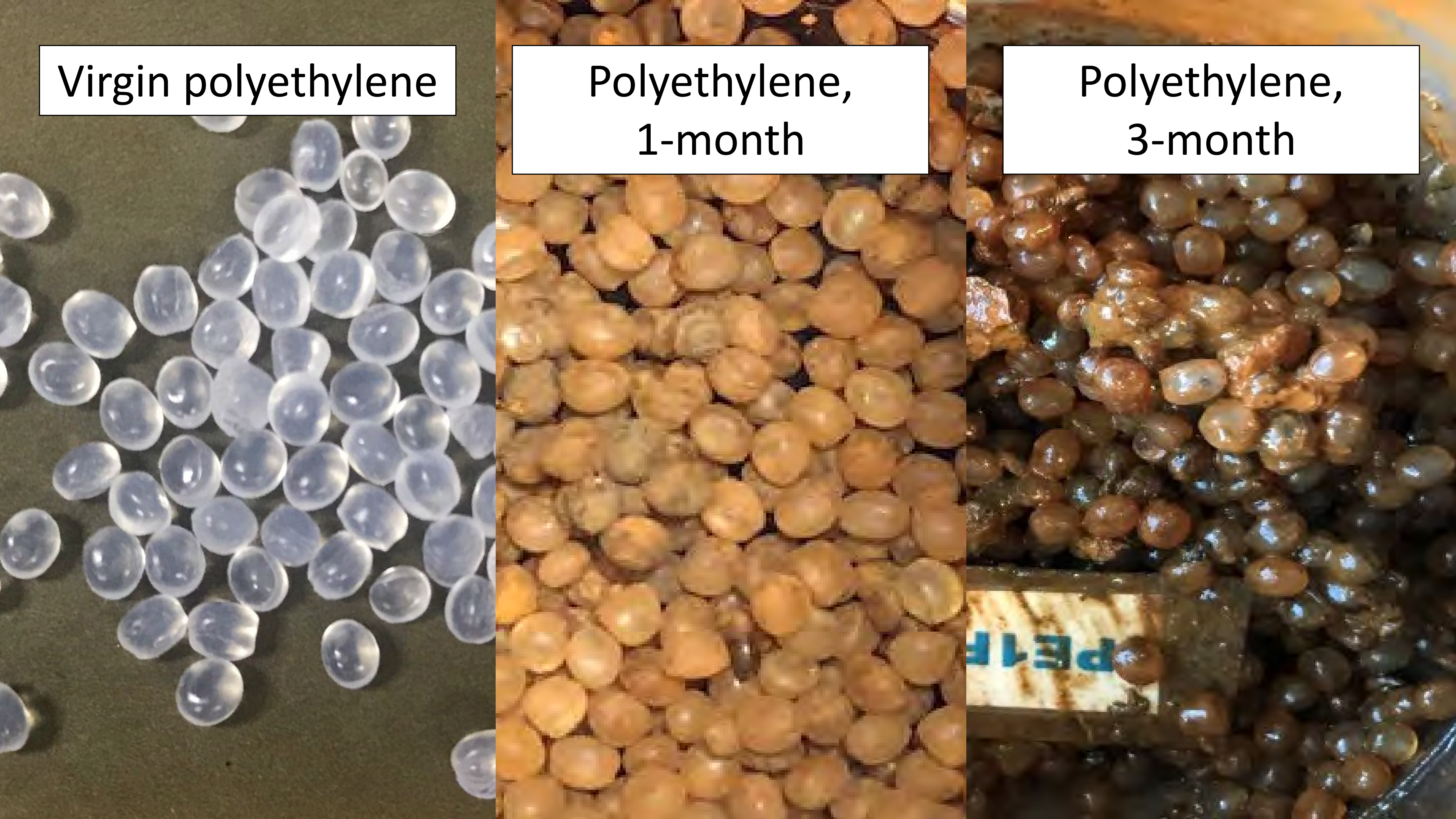
3 - 6
0 - 3
0
0.5
1
2
Kilometers
N

Research Questions Addressed

- Does exposure duration influence adsorption of chemical pollutants and biofilm formation?


Virgin polyethylene
Polyethylene, 1-month
Polyethylene, 3-month

Research Questions Addressed

- Does exposure duration influence adsorption of chemical pollutants and biofilm formation?

- Is plastic type an important factor in accumulation of chemical contaminants and biofilms?

- What role does location play in accumulation of chemical contaminants and biofilms?

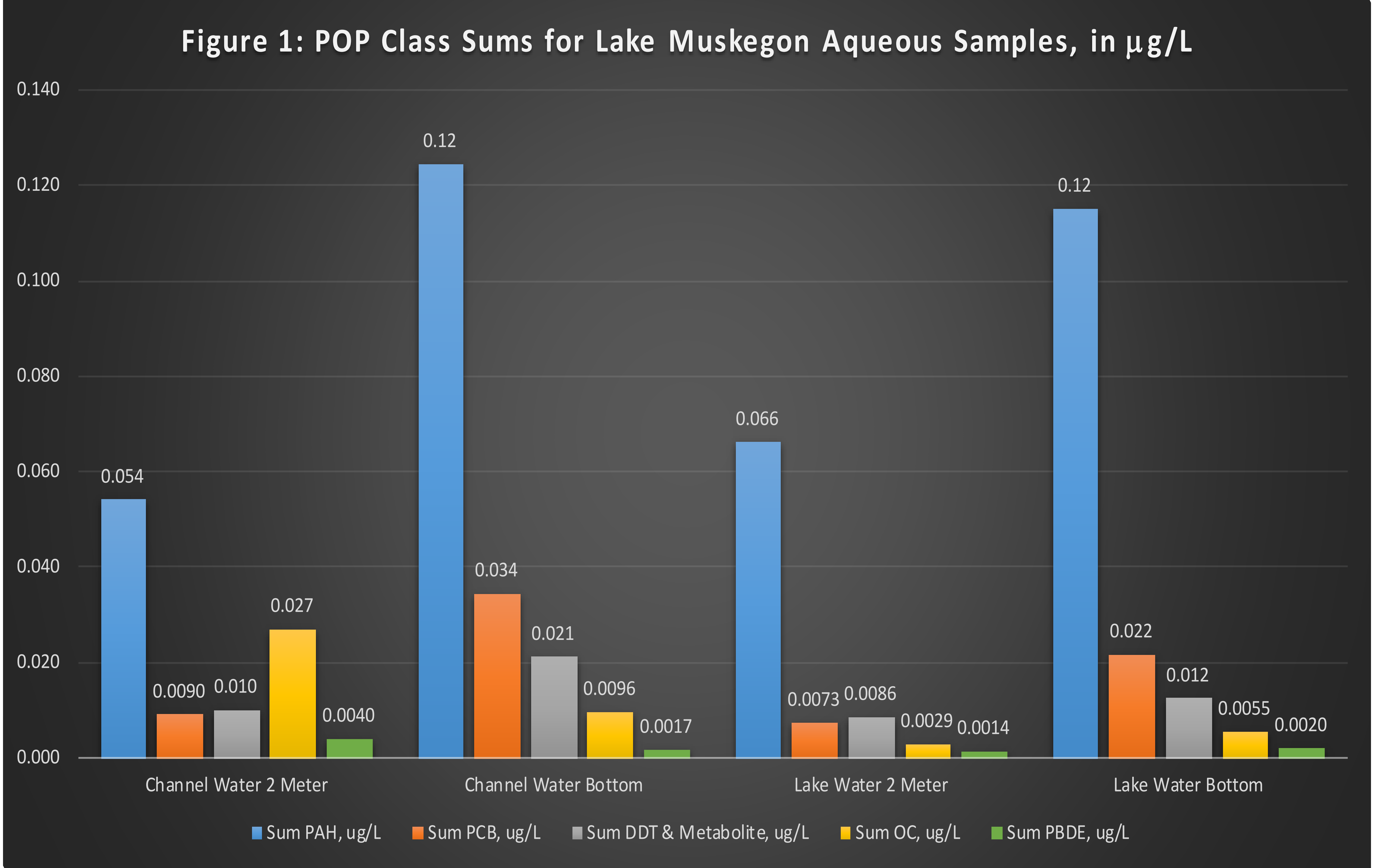
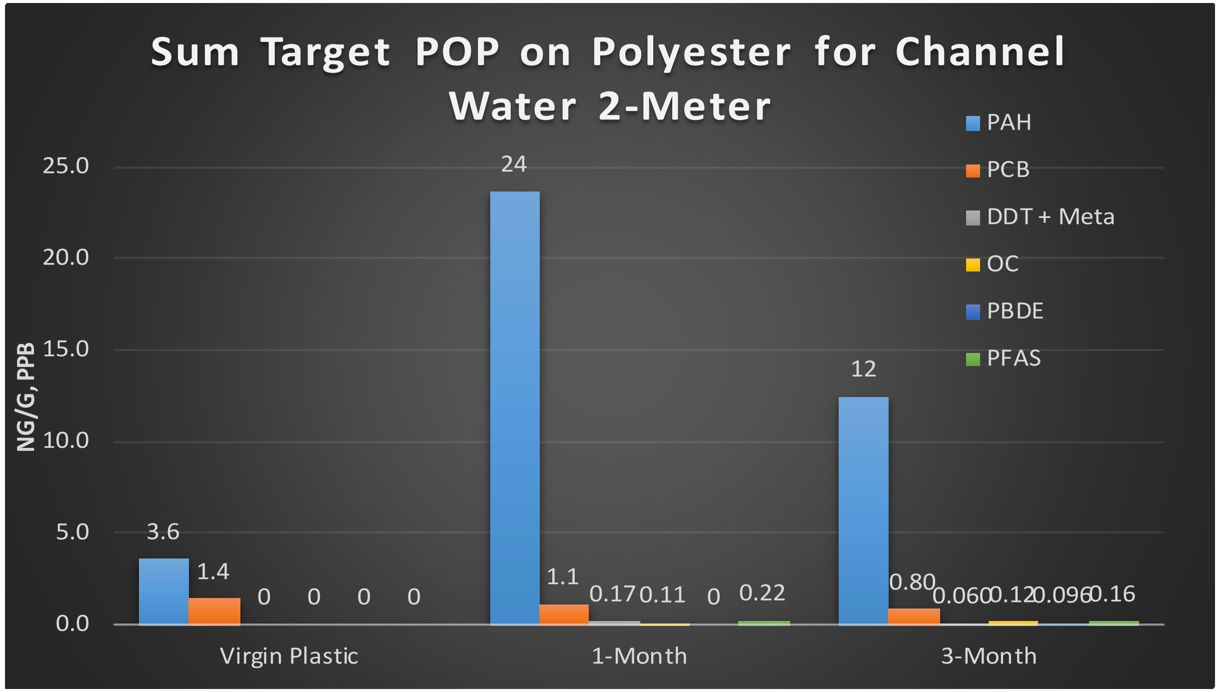
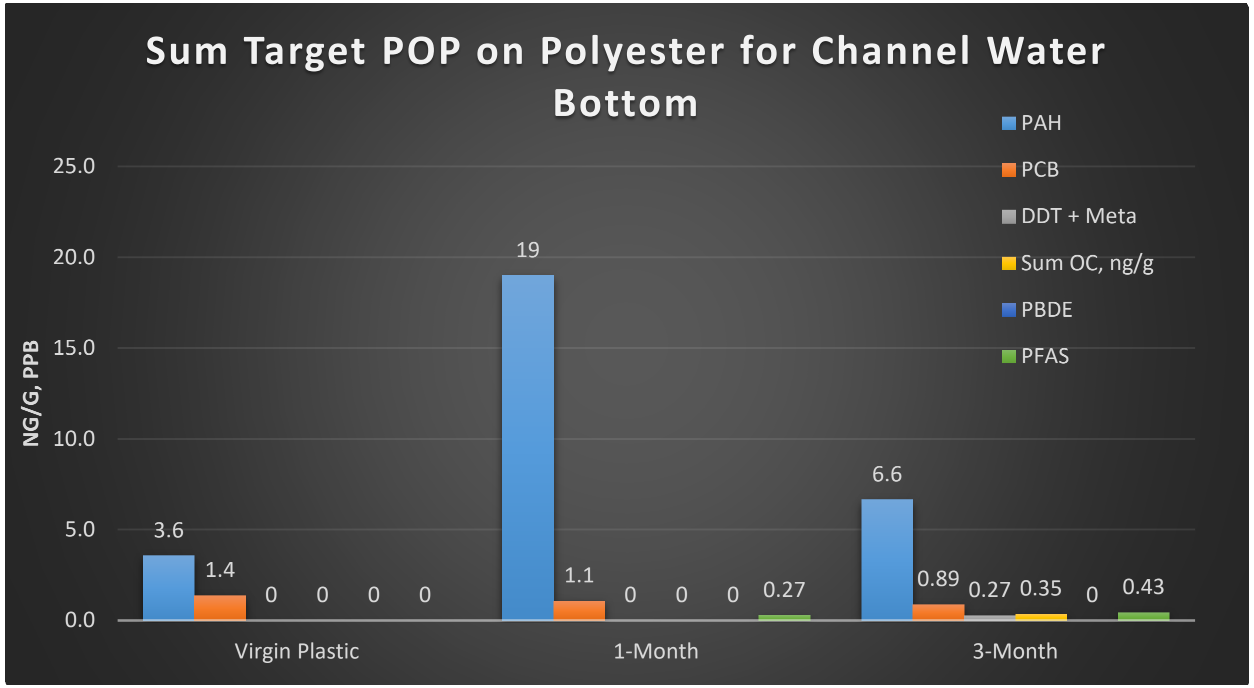
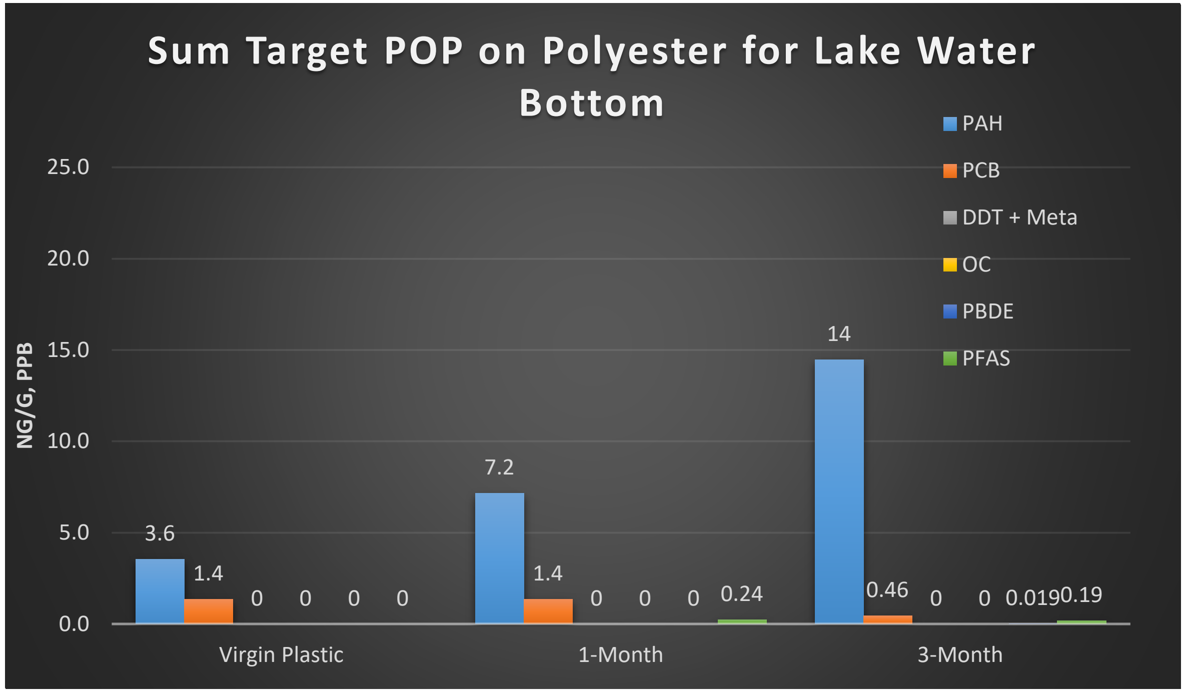
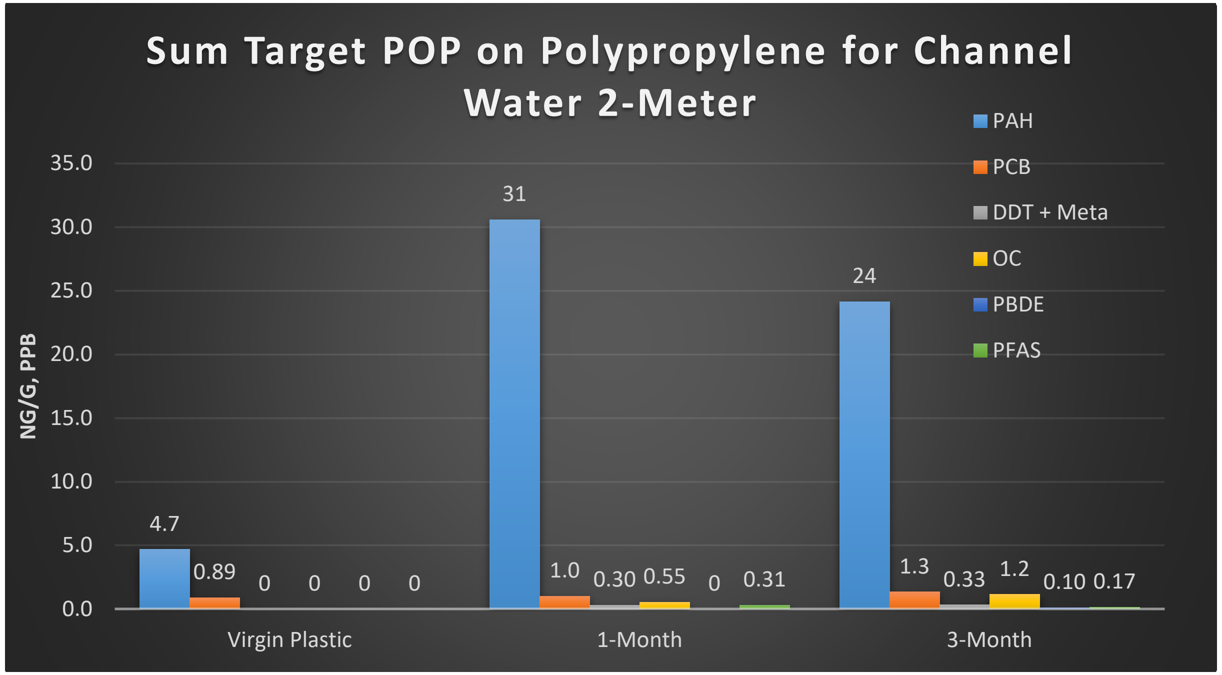


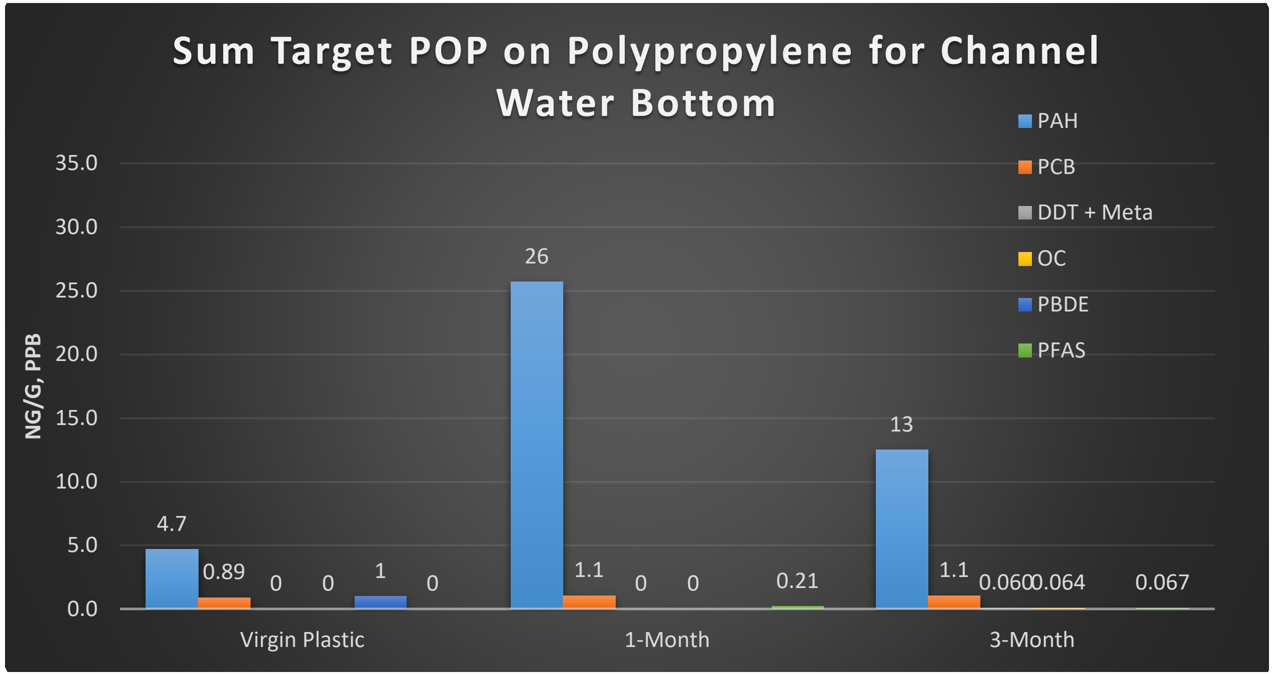
Figure 1: POP Class Sums for Lake Muskegon Aqueous Samples, in µg/L
0.140
0.120
0.100
0.080
0.060
0.040
0.020
0.000
0.054
0.0090
0.010
0.027
0.0040
0.12
0.034
0.021
0.0096
0.0017
0.066
0.0073
0.0086
0.0029
0.0014
0.12
0.022
0.012
0.0055
0.0020
Channel Water 2 Meter
Channel Water Bottom
Lake Water 2 Meter
Lake Water Bottom
Sum PAH, ug/L
Sum PCB, ug/L
Sum DDT & Metabolite, ug/L
Sum OC, ug/L
Sum PBDE, ug/L

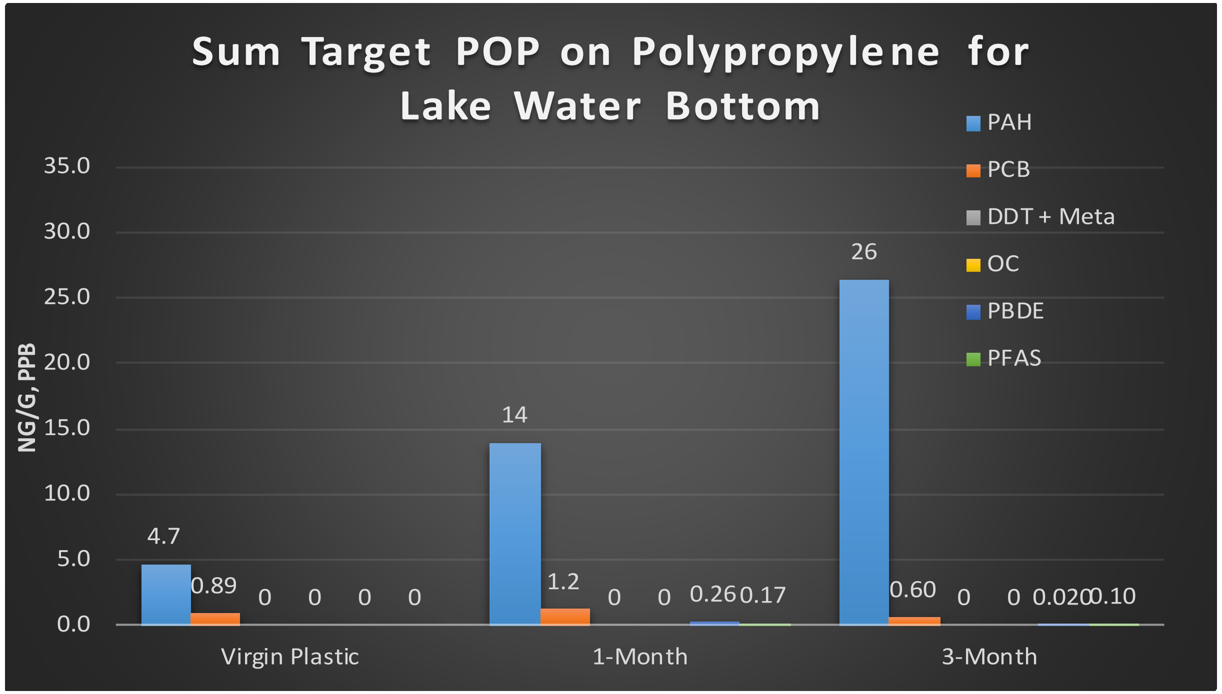

Sum Target POP on Polyester for Channel Water 2-Meter
NG/G, PPB
25.0
20.0
15.0
10.0
5.0
0.0
PAH
PCB
DDT + Meta
OC
PBDE
PFAS
3.6 1.4 0 0 0 0
24 1.1 0.17 0.11 0 0.22
12 0.80 0.060 0.12 0.096 0.16
Virgin Plastic
1-Month
3-Month

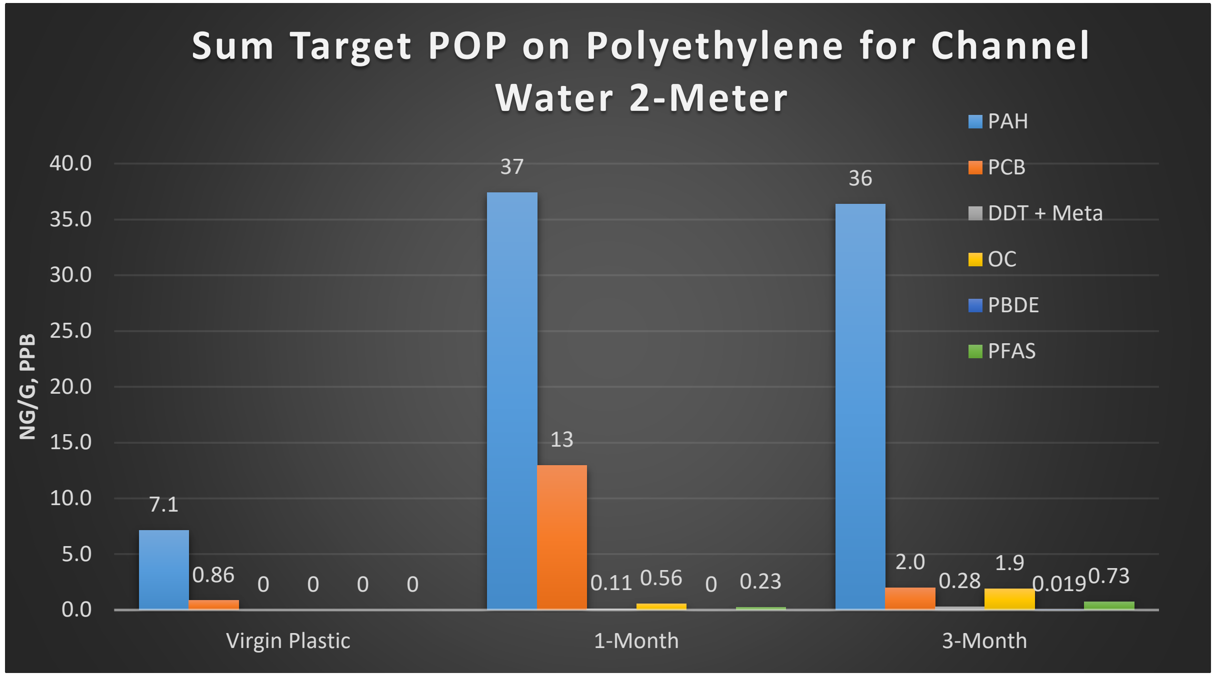

Sum Target POP on Polyester for Channel Water Bottom
NG/G, PPB
25.0
20.0
15.0
10.0
5.0
0.0
PAH
PCB
DDT + Meta
Sum OC, ng/g
PBDE
PFAS
3.6 1.4 0 0 0 0
19 1.1 0 0 0 0.27
6.6 0.89 0.27 0.35 0 0.43
Virgin Plastic
1-Month
3-Month

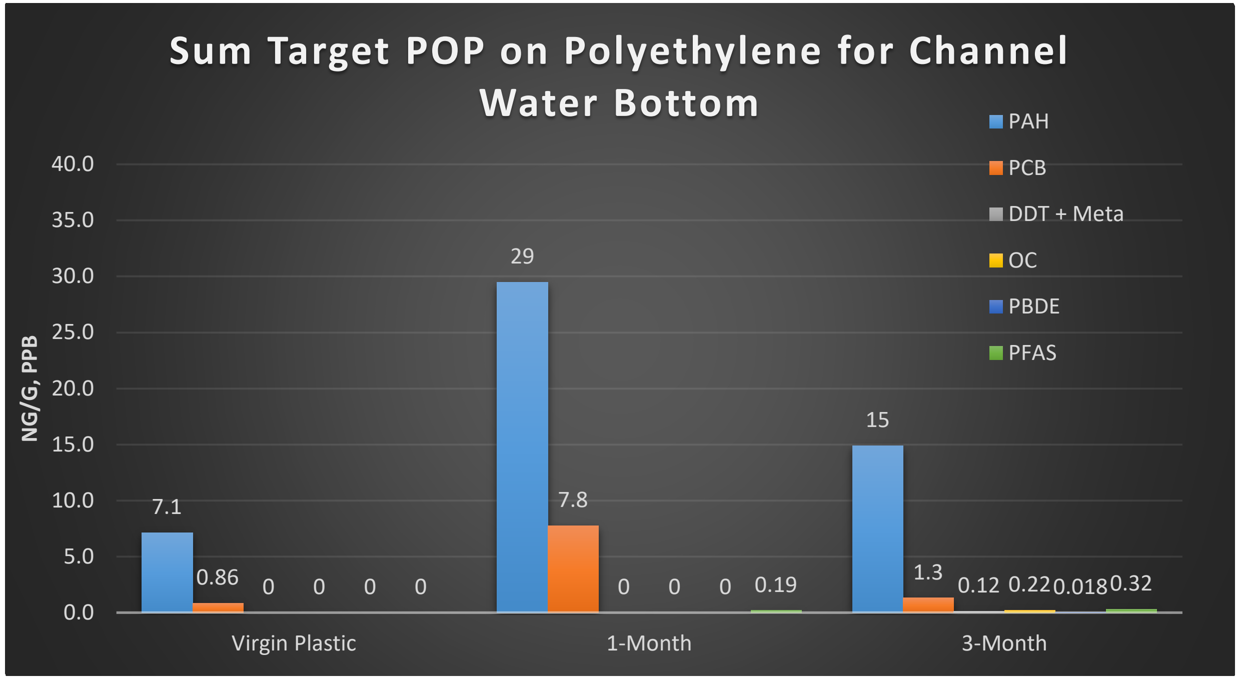

Sum Target POP on Polyester for Lake Water Bottom
NG/G, PPB
25.0
20.0
15.0
10.0
5.0
0.0
PAH
PCB
DDT + Meta
OC
PBDE
PFAS
3.6 1.4 0 0 0 0
7.2 1.4 0 0 0 0.24
14 0.46 0 0 0.019 0.19
Virgin Plastic
1-Month
3-Month

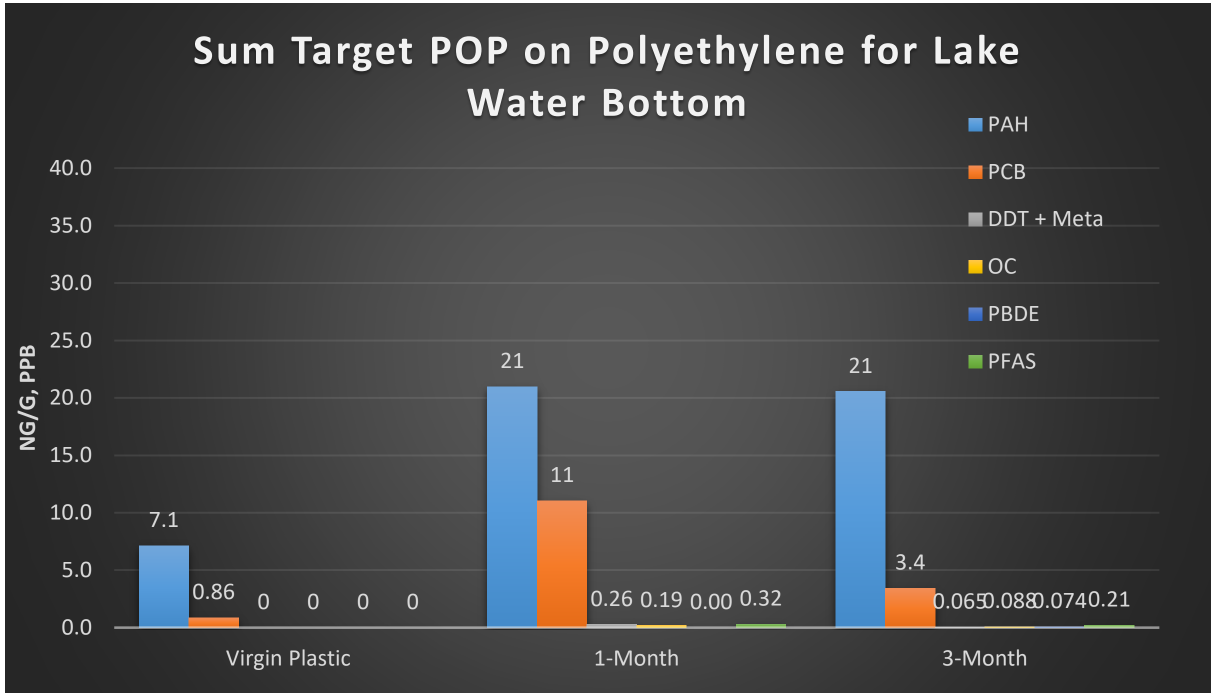

Sum Target POP on Polypropylene for Channel Water 2-Meter
PAH
PCB
DDT + Meta
OC
PBDE
PFAS
NG/G, PPB
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0.0
4.7
0.89
0
0
0
0
31
1.0
0.30
0.55
0
0.31
24
1.3
0.33
1.2
0.10
0.17
Virgin Plastic
1-Month
3-Month


Sum Target POP on Polypropylene for Channel Water Bottom
PAH
PCB
DDT + Meta
OC
PBDE
PFAS
NG/G, PPB
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0.0
4.7
0.89
0
0
1
0
26
1.1
0
0
0.21
13
1.1
0.060
0.064
0.067
Virgin Plastic
1-Month
3-Month


Sum Target POP on Polypropylene for Lake Water Bottom
PAH
PCB
DDT + Meta
OC
PBDE
PFAS
NG/G, PPB
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0.0
4.7
0.89
0
0
0
0
14
1.2
0
0
0.26
0.17
26
0.60
0
0
0.020
0.10
Virgin Plastic
1-Month
3-Month

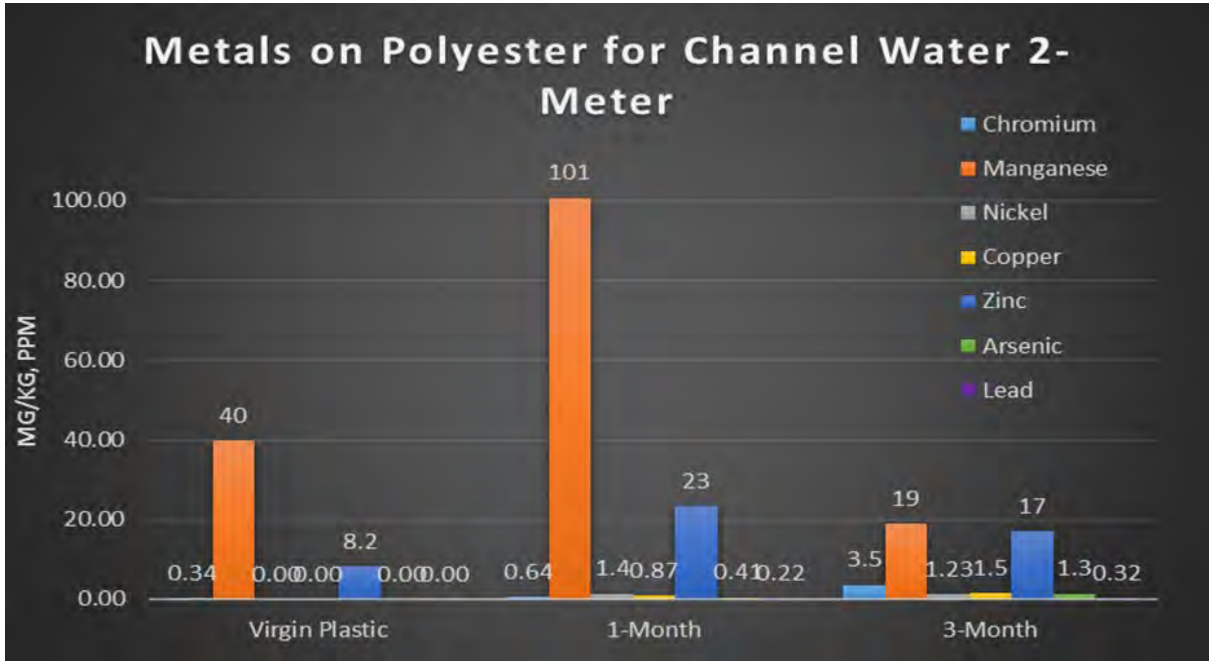

Sum Target POP on Polyethylene for Channel Water 2-Meter
PAH
PCB
DDT + Meta
OC
PBDE
PFAS
NG/G, PPB
40.0
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0.0
7.1
0.86
0
0
0
0
37
13
0.11
0.56
0
0.23
36
2.0
0.28
1.9
0.019
0.73
Virgin Plastic
1-Month
3-Month

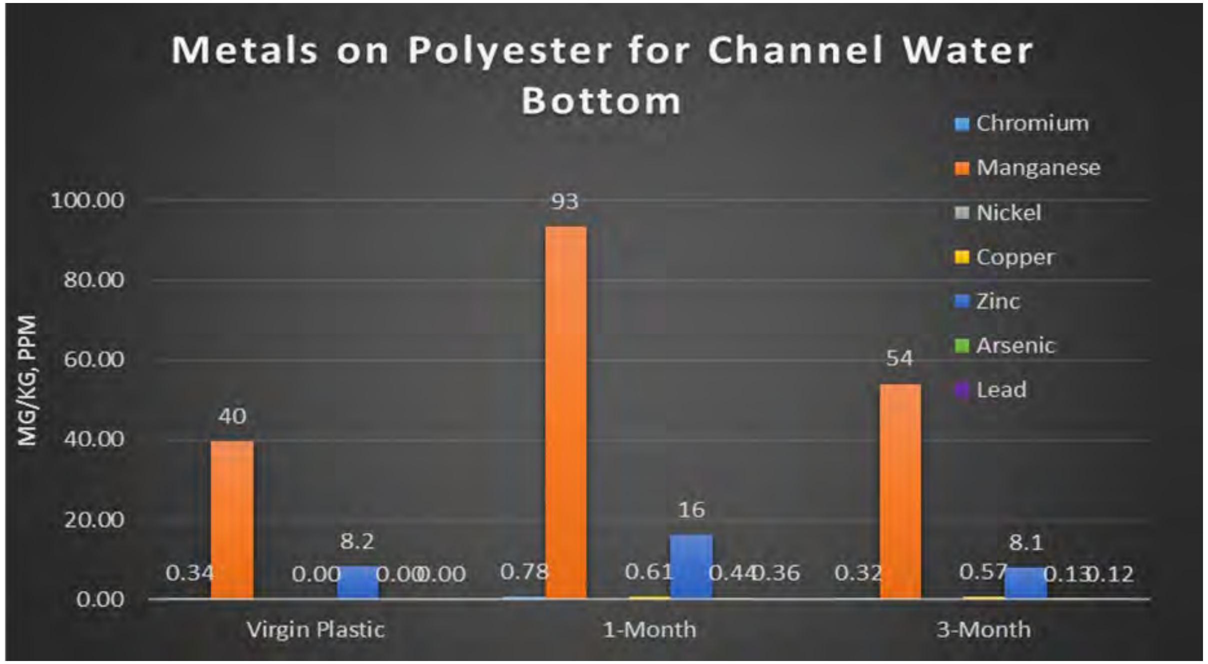

Sum Target POP on Polyethylene for Channel Water Bottom
PAH
PCB
DDT + Meta
OC
PBDE
PFAS
NG/G, PPB
40.0
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0.0
7.1
0.86
0
0
0
0
29
7.8
0
0
0
0.19
15
1.3
0.12
0.22
0.018
0.32
Virgin Plastic
1-Month
3-Month


Sum Target POP on Polyethylene for Lake Water Bottom
PAH
PCB
DDT + Meta
OC
PBDE
PFAS
NG/G, PPB
40.0
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0.0
7.1
0.86
0
0
0
0
21
11
0.26
0.19
0.00
0.32
21
3.4
0.065
0.088
0.074
0.21
Virgin Plastic
1-Month
3-Month

POP Results

- POP concentrations from highest to lowest: polyethylene > polypropylene > polyester.
- PAHs were the most prevalent POP found on the microplastics. Channel sample concentrations peaked at 1-mo, then declined at 3-mo; lake bottom samples→ reverse
- Only slight concentrations of DDT, DDE, DDD, PBDEs, and PFAS were found on plastics after 1-mo and 3-mo deployments.


Metals on Polyester for Channel Water 2-Meter
Chromium
Manganese
Nickel
Copper
Zinc
Arsenic
Lead
MG/KG, PPM
100.00
80.00
60.00
40.00
20.00
0.00
40
0.34
0.00
0.00
8.2
0.00
0.00
101
0.64
1.4
0.87
23
0.41
0.22
19
3.5
1.23
1.5
17
1.3
0.32
Virgin Plastic
1-Month
3-Month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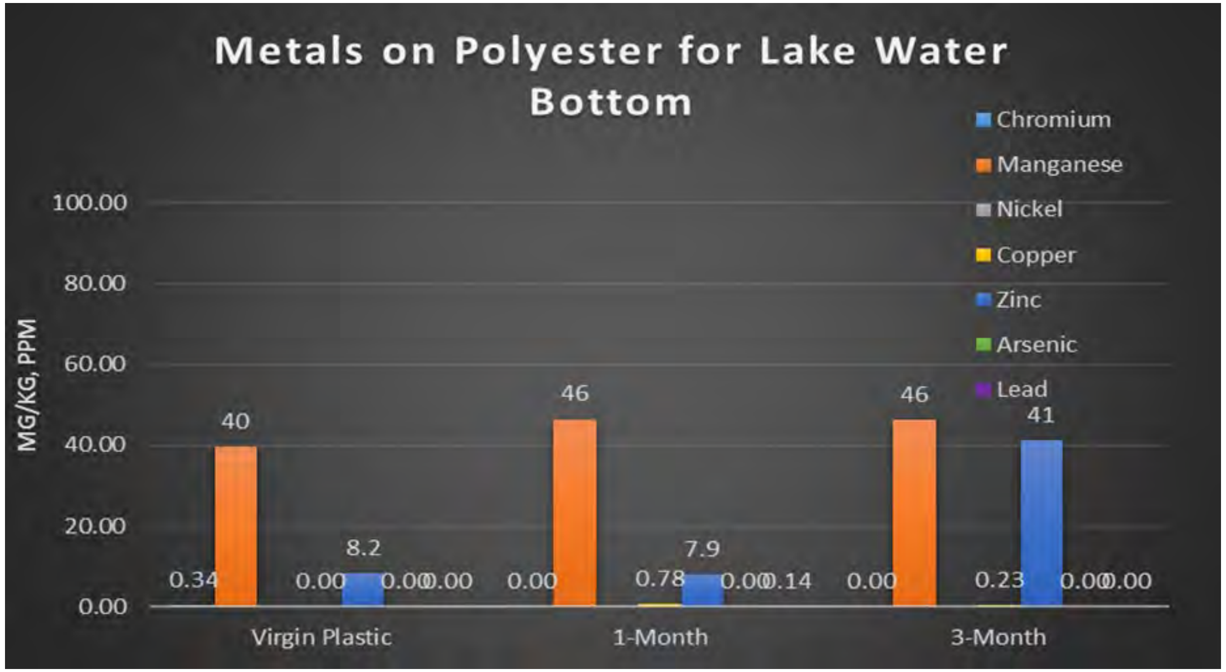
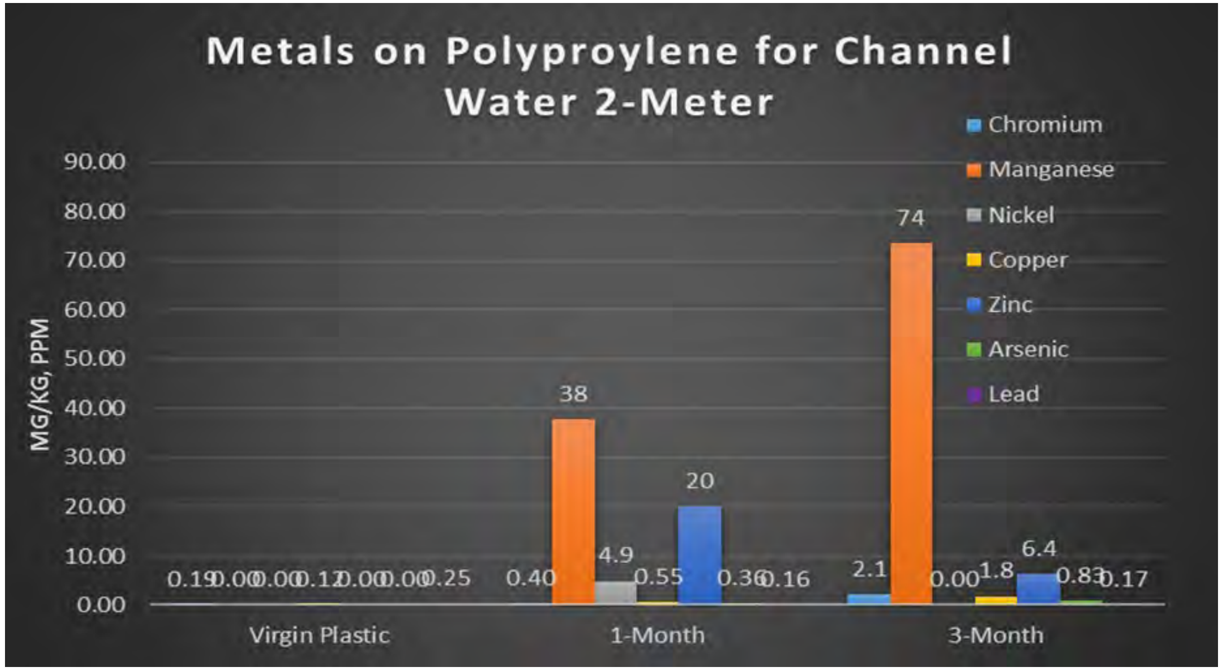
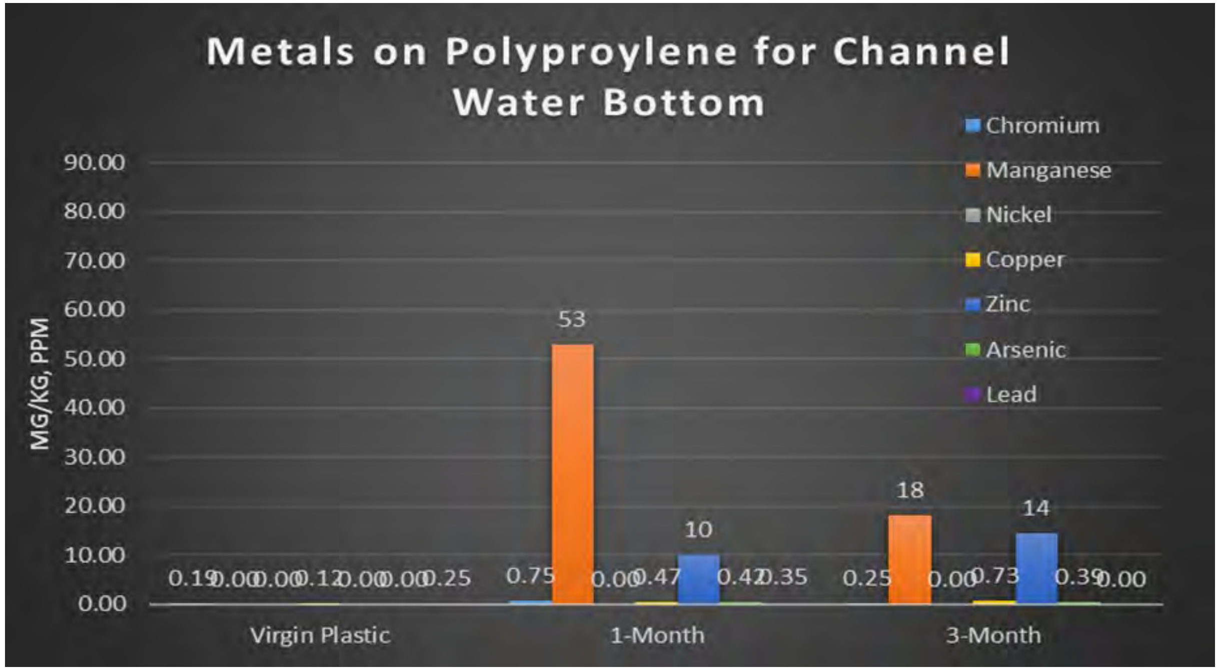
Chromium
Manganese
Nickel
Copper
Zinc
Arsenic
Lead
MG/KG, PPM
100.00
80.00
60.00
40.00
20.00
0.00
40
0.34
0.00
8.2
0.00
0.00
93
0.78
0.61
16
0.44
0.36
54
0.32
0.57
8.1
0.13
0.12
Virgin Plastic
1-Month
3-Month


Metals on Polyester for Lake Water Bottom
Chromium
Manganese
Nickel
Copper
Zinc
Arsenic
Lead
MG/KG, PPM
100.00
80.00
60.00
40.00
20.00
0.00
40
0.34
0.00
8.2
0.00
0.00
46
0.00
0.78
7.9
0.00
0.14
46
0.00
0.23
41
0.00
0.00
Virgin Plastic
1-Month
3-Month


Metals on Polyproylene for Channel Water 2-Meter
Chromium
Manganese
Nickel
Copper
Zinc
Arsenic
Lead
MG/KG, PPM
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0.19 0.00 0.00 0.12 0.00 0.00 0.25
0.40 38 4.9 0.55 20 0.36 0.16
2.1 74 0.00 1.8 6.4 0.83 0.17
Virgin Plastic
1-Month
3-Month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Chromium
Manganese
Nickel
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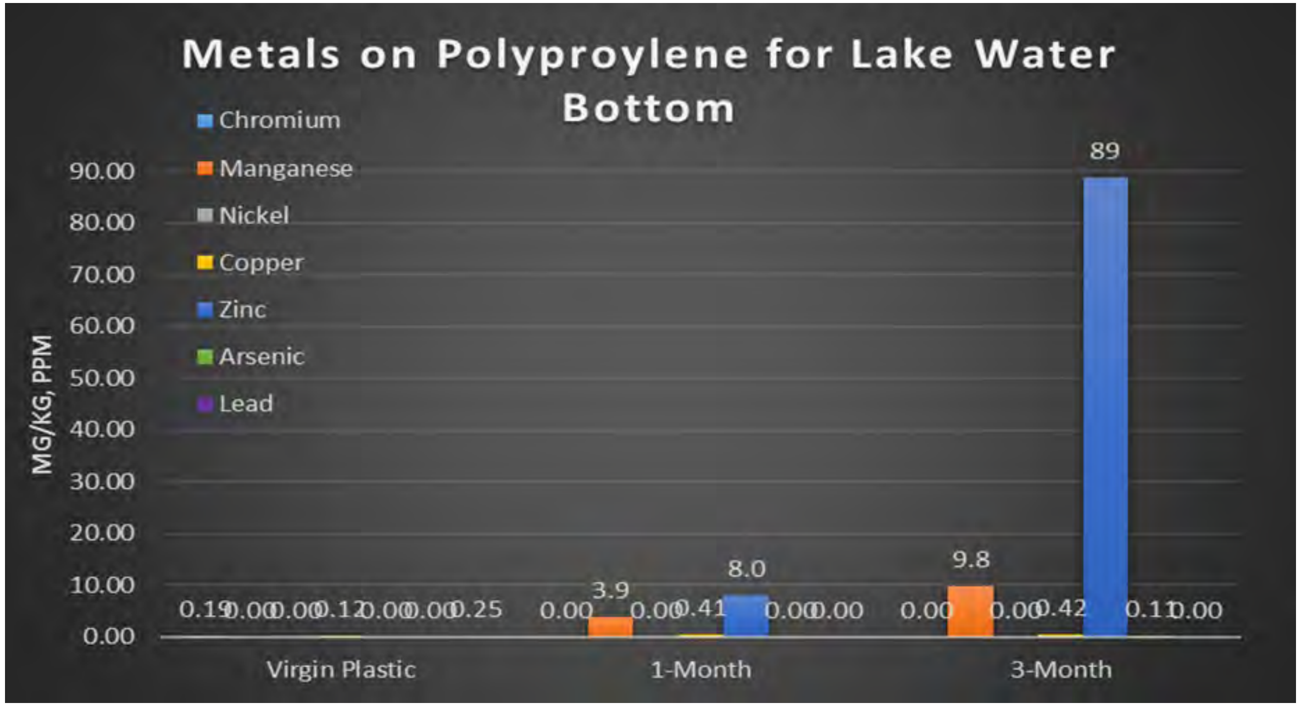
Zinc
Arsenic
Lead
MG/KG, PPM
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0.19 0.00 0.00 0.12 0.00 0.00 0.25
0.75 53 0.00 0.47 10 0.42 0.35
0.25 18 0.00 0.73 14 0.39 0.00
Virgin Plastic
1-Month
3-Month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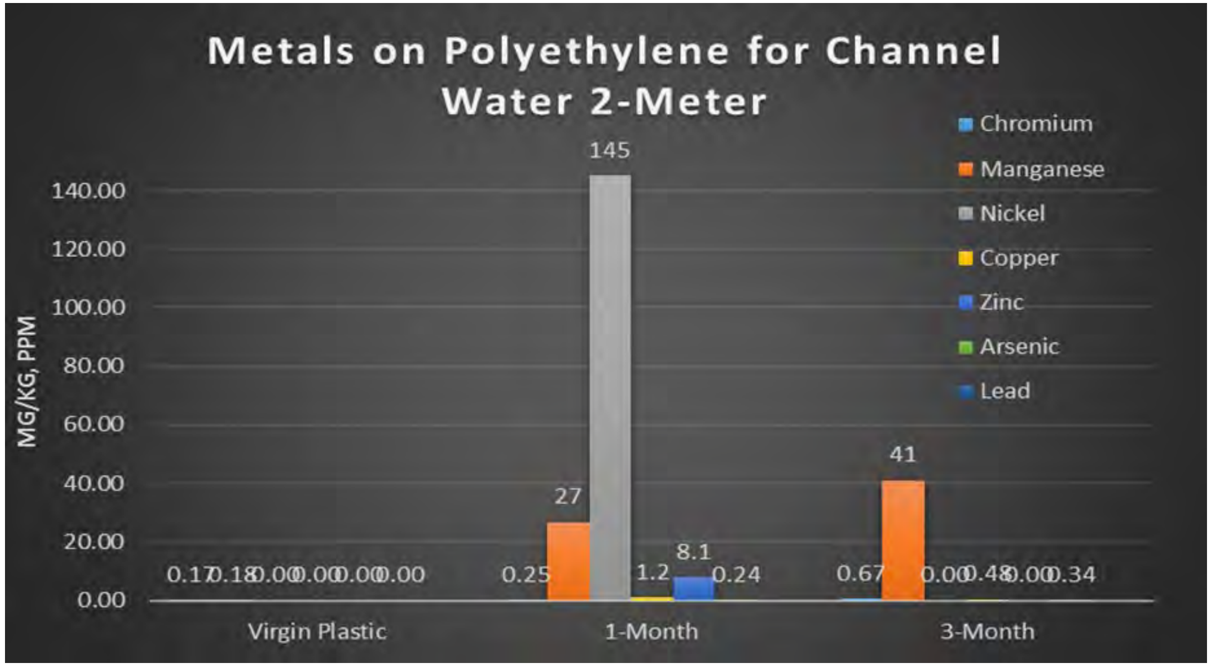
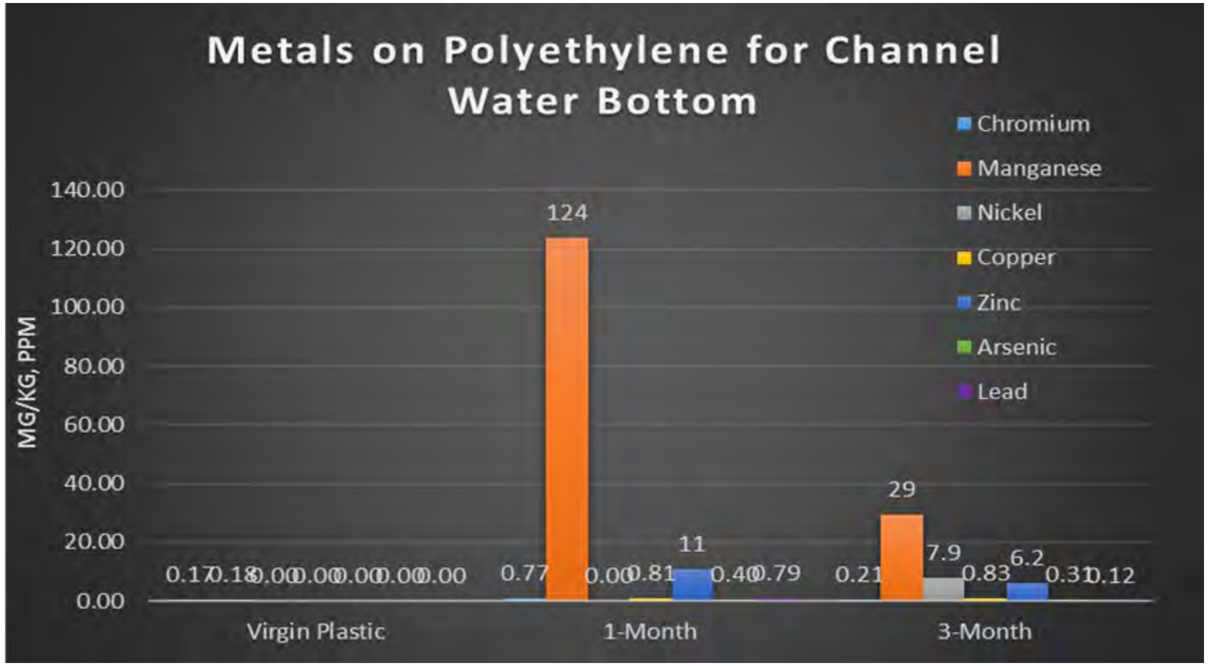
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0.19 0.00 0.00 0.12 0.00 0.00 0.25
0.00 3.9 0.00 0.41 8.0 0.00 0.00
0.00 9.8 0.00 0.42 89 0.11 0.00
Virgin Plastic
1-Month
3-Month


Metals on Polyethylene for Channel Water 2-Meter
Chromium
Manganese
Nickel
Copper
Zinc
Arsenic
Lead
MG/KG, PPM
0.00
20.00
40.00
60.00
80.00
100.00
120.00
140.00
0.17 0.18 0.00 0.00 0.00 0.00
0.25
27
145
1.2
8.1
0.24
0.67
41
0.00 0.48 0.00 0.34
Virgin Plastic
1-Month
3-Month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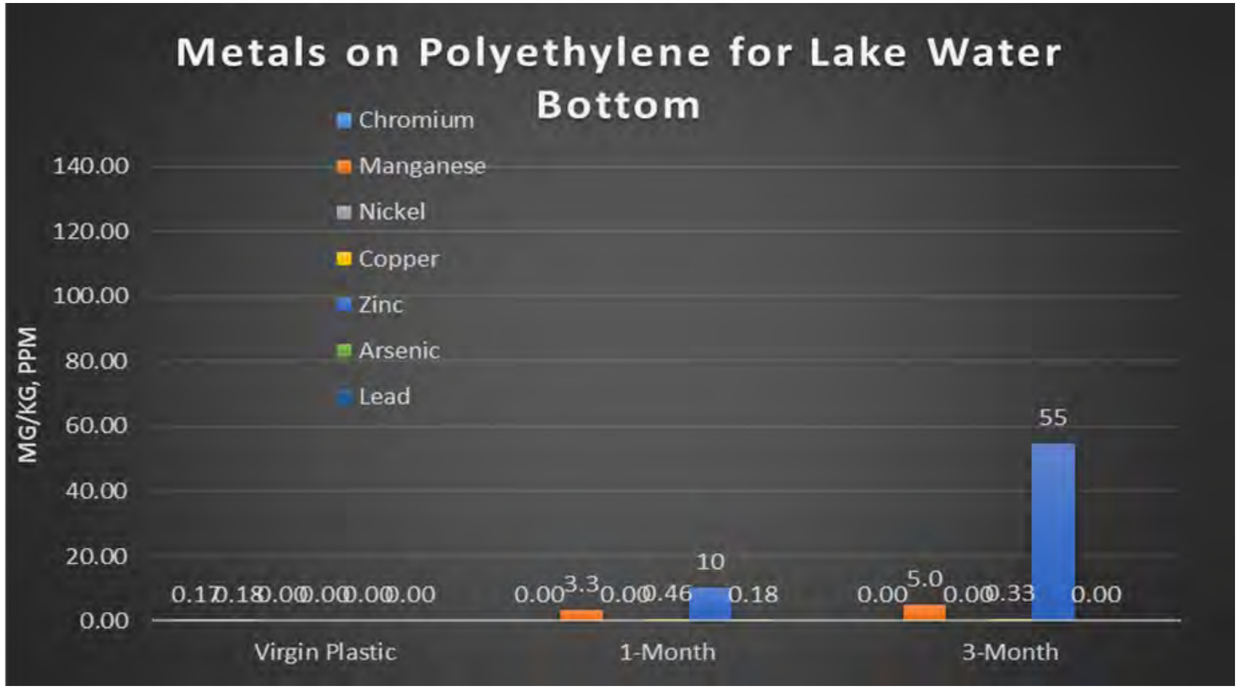
Copper
Zinc
Arsenic
Lead
MG/KG, PPM
0.00
20.00
40.00
60.00
80.00
100.00
120.00
140.00
0.17 0.18 0.00 0.00 0.00 0.00 0.00
0.77
124
0.00 0.81
11
0.40 0.79
0.21
29
7.9
0.83
6.2
0.31 0.12
Virgin Plastic
1-Month
3-Month


Metals on Polyethylene for Lake Water Bottom
Chromium
Manganese
Nickel
Copper
Zinc
Arsenic
Lead
MG/KG, PPM
0.00
20.00
40.00
60.00
80.00
100.00
120.00
140.00
0.17 0.18 0.00 0.00 0.00 0.00
0.00
3.3
0.00 0.46
10
0.18
0.00
5.0
0.00 0.33
55
0.00
Virgin Plastic
1-Month
3-Month

Metals Results

- Significant concentrations of manganese, and to a lesser degree zinc, were observed on the polyester material before deployment (manufacturing or processing artefact?)

- Mn and Zn were the most abundant metals after deployment.

- Like the POPs, 4 out of 6 of the channel water metals concentrations spiked at 1-month and then declined at 3-months.

PFAS Results

- Most common PFAS's were PFHxA, PFHpA, and PFOA
- Background water sample concentrations low:
  - Channel (surface): 2.8 ng/L (ppt)
  - Lake (surface): 3.3 ng/L (ppt)
- PFAS's were concentrated 24 to 259× background water samples PFAS concentrations very variable, suggesting effect of biofilm

Summary

- Within 1-month, certain microplastics concentrated specific POPs up to 380 × aqueous background concentration.
- Mn and Zn were concentrated at a minimum of 90 to 600 × aqueous background concentrations.
- POP and metals adsorption varied temporally and spatially at the locations of this study.
- PFAS also concentrated but overall impact to fish likely minimal

Next Steps

- Publish findings
- Further work on PFAS
- Feeding experiments:
    - Dreissenid mussels
    - Yellow perch

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Sampler Design

- Maggie Oudsema (AWRI)

Sampler Fabrication, Deployment, and Retrieval

- Emily Kindervater, Rachel Orzechowski, Paige Kleindl, & Mike Hassett (AWRI)

Plastic Preparations, Sample Preparation & Analysis

- Jessica Porter & Kathryn Gunderson (ISTC)

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Questions?

Extra Slides

Sample Preparation – Water Samples

Aqueous Samples (POPs except PFAS)

- Liquid-Liquid extraction with dichloromethane
- Extract drying under sodium sulfate
- Silica gel fractionation
- Exchange to hexane and concentrate to 1.0 mL final volume

Aqueous Samples (PFAS) per US EPA Method 537

- Solid Phase Extraction (SPE) with Agilent Bond Elut-LMS
- Blow to dryness under nitrogen
- Reconstituted to 1.0 ml in methanol-water (96:4)

Sample Preparations

Plastics (POPs except PFAS)

- Accelerated solvent extraction (ASE 300) with hexane
- Silica gel fractionation
- Exchange to hexane and concentrate to 1.0 mL final volume

Plastics (PFAS)

- Solid-Liquid extraction with methanol and centrifugation
- Exchange to 60% ammonia acetate (20mM) : 40% methanol and concentrate to 1.0 mL final volume

Plastics (Metals)

- Microwave digest with nitric acid and dilute to final volume 50 mL in DI water

Associated Quality Control

Per Sample – 18 POP Surrogates and 11 POP internal standards

For PFAS – 7 Isotope PFAS Surrogates and 2 internal standards

- Per Preparation Batch
- All samples prepared in triplicate (except PFAS in duplicates)
- Reagent blank & reagent blank spike
- Silica gel quality control spike (except PFAS)
- Sample matrix spike
- Analytical sample duplicate
- Analytical spike sample

Sample Analysis

PAHs and PCBs

- Shimadzu QP-2010 SE Gas Chromatography Mass Spectrometer

DDT, DDE, DDD, OCs, and PBDEs

- Agilent 6890 Gas Chromatograph coupled to an Autospec Ultima High Resolution Mass Spectrometer

PFAS

- Waters Alliance 2695 coupled to a Quattro Micro tandem mass spectrometer

Metals

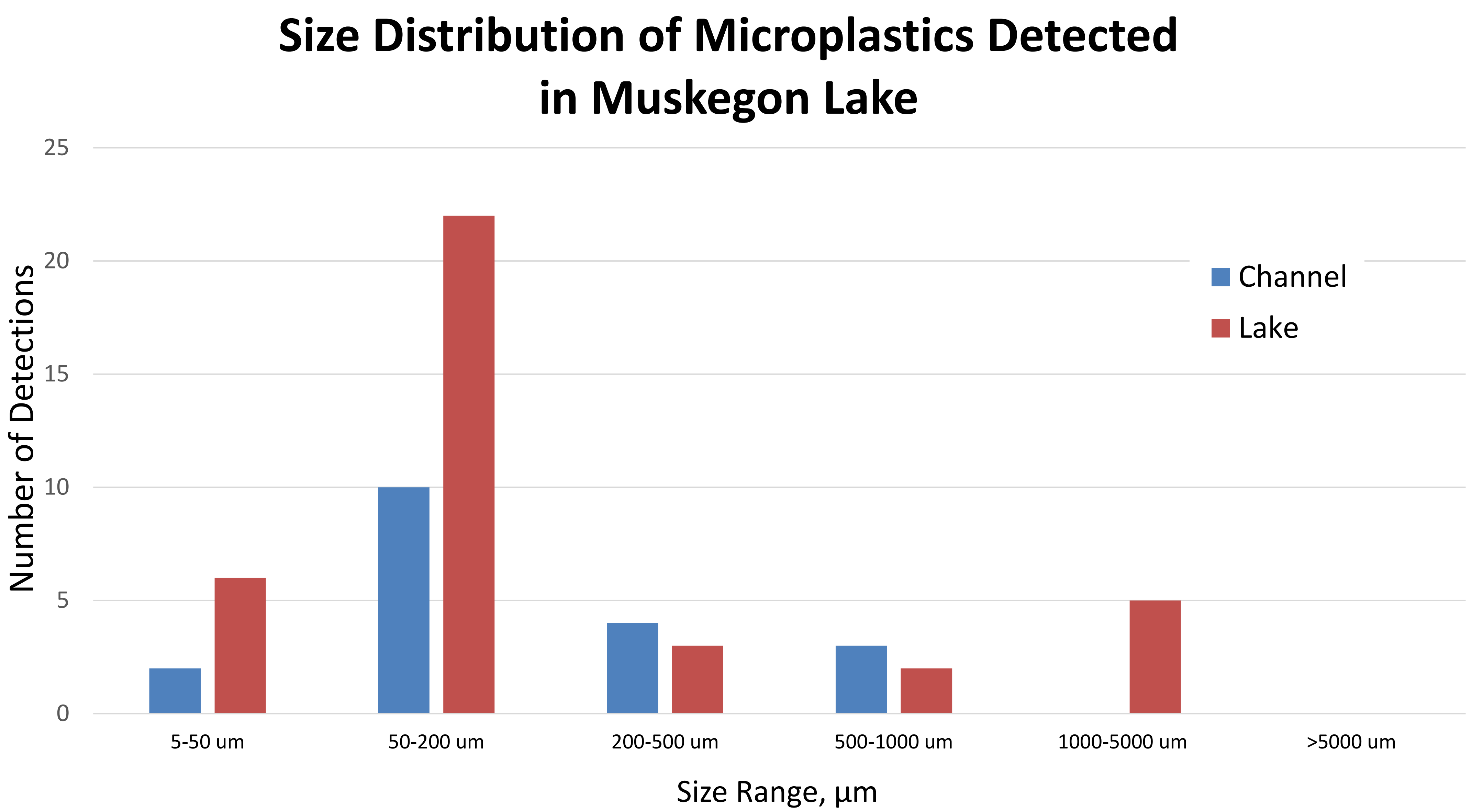
- VG PQ ExCell Inductively coupled plasma mass spectrometer

PFAS Results

- McNeish et al. (2018) found mean of 13 microplastic particles per fish in Muskegon River
- This study showed a PFAS concentration of 0.87 ng/g (worst case)
  - Assuming a 1.5 mm microfiber mass of 1.5×10^{-5} cm^3:

1.5×10^{-5} cm^3 (g/*particle*) × *13 particles* × 0.87 ng/g = 0.0002 ng

- Unlikely to have negative effect on fish (but need info on feeding; interactions with POPs; commercial microplastics)


Size Distribution of Microplastics Detected
in Muskegon Lake
25
20
15
10
5
0
Number of Detections
Channel
Lake
5-50 um
50-200 um
200-500 um
500-1000 um
1000-5000 um
>5000 um
Size Range, µm