Adsorption of PFAS and Microcystins by Virgin and Weathered Microplastics

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DRINKING WATER RESEARCH GROUP

Microplastics:

Defined as polymeric particles
1 nm - 5 mm in size

Potential human health hazards:

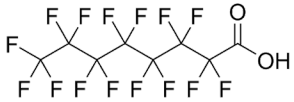
1) Physical – Due to small size
2) Chemical – Due to chemical additives
   + adsorption of contaminants (PFAS) present in Lakes & Rivers
3) Biological – Due to biofilm formation
   + adsorption of biotoxins (microcystins)


Microbeads

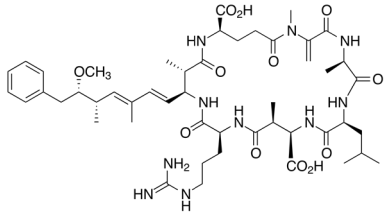
Microplastics:

Serve as potential transport vectors for contaminants (in drinking water)

- Per- and Polyfluoroalkyl Substances (PFAS)



- Microcystins



Microplastics - not fully removed by drinking water treatment

- Potential route for human exposure

Natural weathering of microplastics – alters surface characteristics

- Potential impact on adsorption behaviour

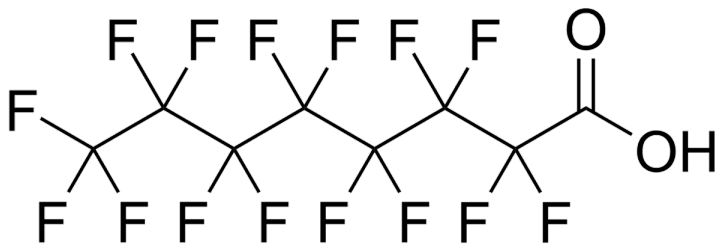
Per- and Polyfluoroalkyl Substances (PFAS):

- Group of emerging contaminants
- Extensive applications:
  - Fire-fighting, packaging, electronics, etc.
  - Also used as additives for plastics
- Persistent properties - "*Forever Chemicals*"
- Found in many consumer products
- Human health risks:
  - Thyroid disease
  - Immune & reproductive system issues
  - Potential cancer

Per- and Polyfluoroalkyl Substances (PFAS):

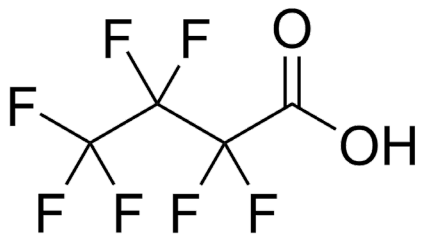
- Interest *shifting* from long- to short-chain PFAS

Long-chain PFAS



- Dominant use (previously)
- Health advisory limits established:
  - PFOA: 0.004 ng/L
  - PFOS: 0.02 ng/L

Short-chain PFAS



- Increasing use
- Studies lacking
- Higher health advisory levels:
  - PFBS: 2,000 ng/L

Microcystins:

Climate Change

→ Eutrophication

→ Algal blooms

→ Microcystins

- Severe health impacts:
  - Toxic to liver and kidney cells
  - Regulated in drinking water in many jurisdictions

Objectives:

Examine:

1) Adsorption of PFAS and microcystins - by microplastics in freshwater matrices.

2) Impact of weathering of microplastics on adsorption.

Overall Experimental Design:

2 short-chain PFAS (PFBA, PFBS) & 2 long-chain PFAS (PFOA, PFOS) (500 ng/L)

Perfluorobutanoic acid (PFBA)
Perfluorobutanesulfonic acid (PFBS)

Perfluorooctanoic acid (PFOA)
Perfluorooctane sulfonate (PFOS)

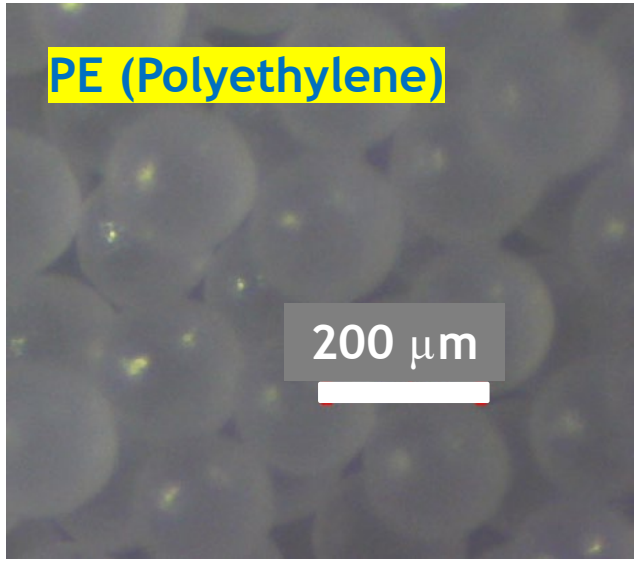
2 common microcystins: Microcystin (MC) -LR and -RR (50 µg/L)

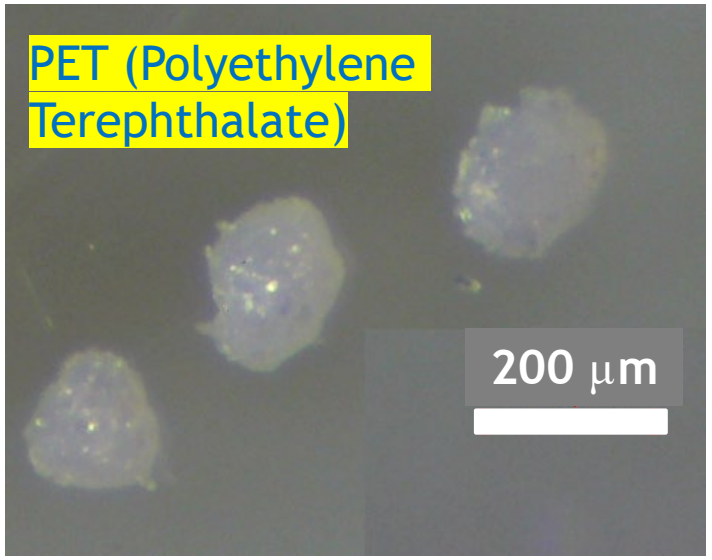
5 different types microplastics: PE/LDPE, PET, PS, PMMA, PVC

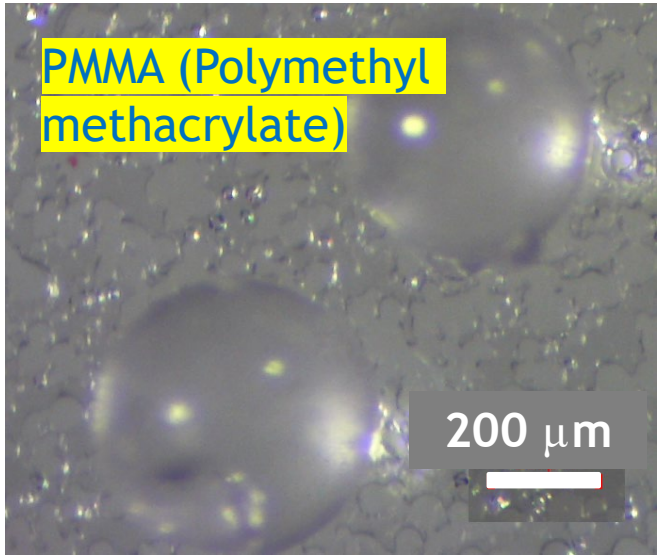
Polyethylene (PE) / Low Density PE (LDPE)
Polyethylene Terephthalate (PET)
Polystyrene (PS)
Poly(methyl methacrylate) (PMMA)
Polyvinyl Chloride (PVC)

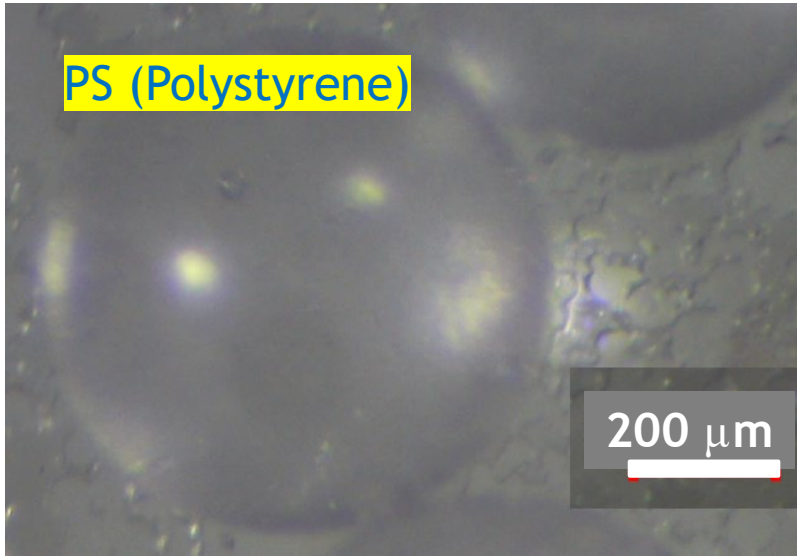
Artificial Fresh Water (AFW)

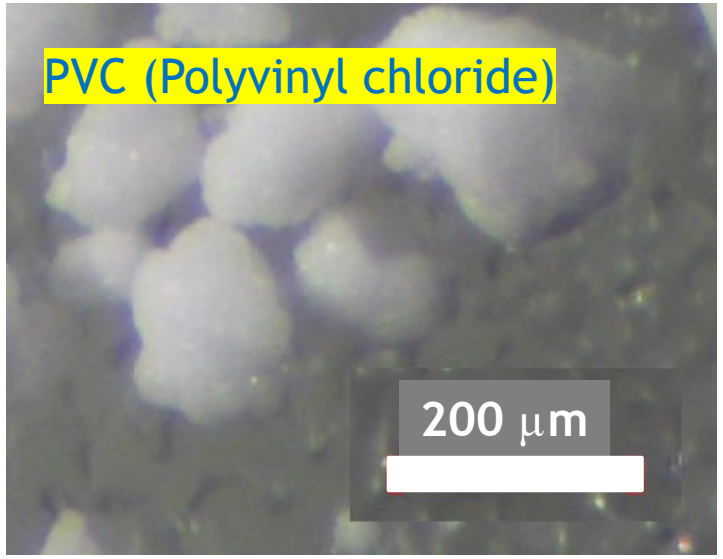
(Milli-Q water + KCl + $CaCl_2$ + $NaHCO_3$ + $MgSO_4$ + bio-inhibitor)


PE (Polyethylene)
200 µm


PET (Polyethylene Terephthalate)
200 µm


PMMA (Polymethyl methacrylate)
200 µm


PS (Polystyrene)
200 µm

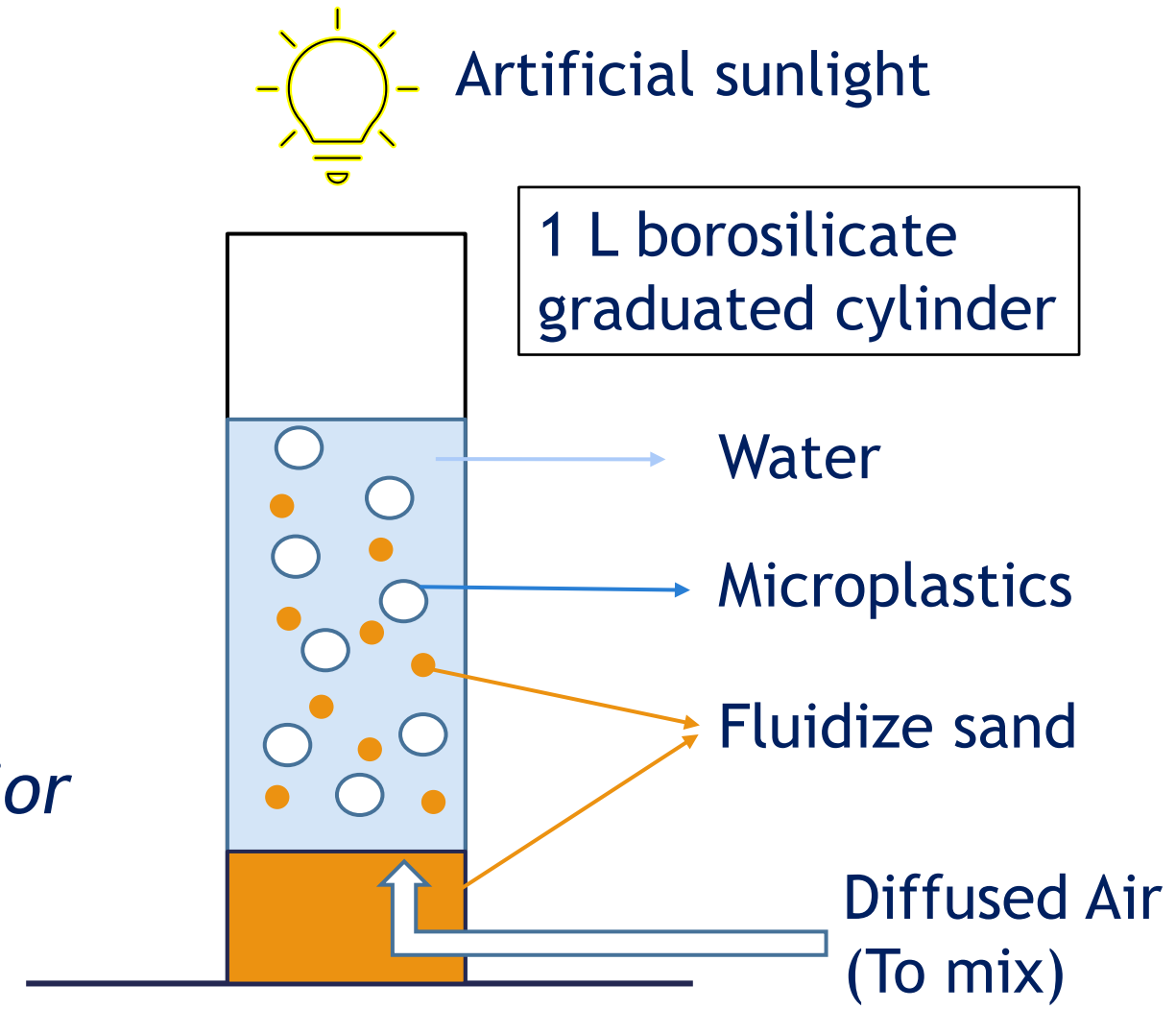

PVC (Polyvinyl chloride)
200 µm

Weathering:

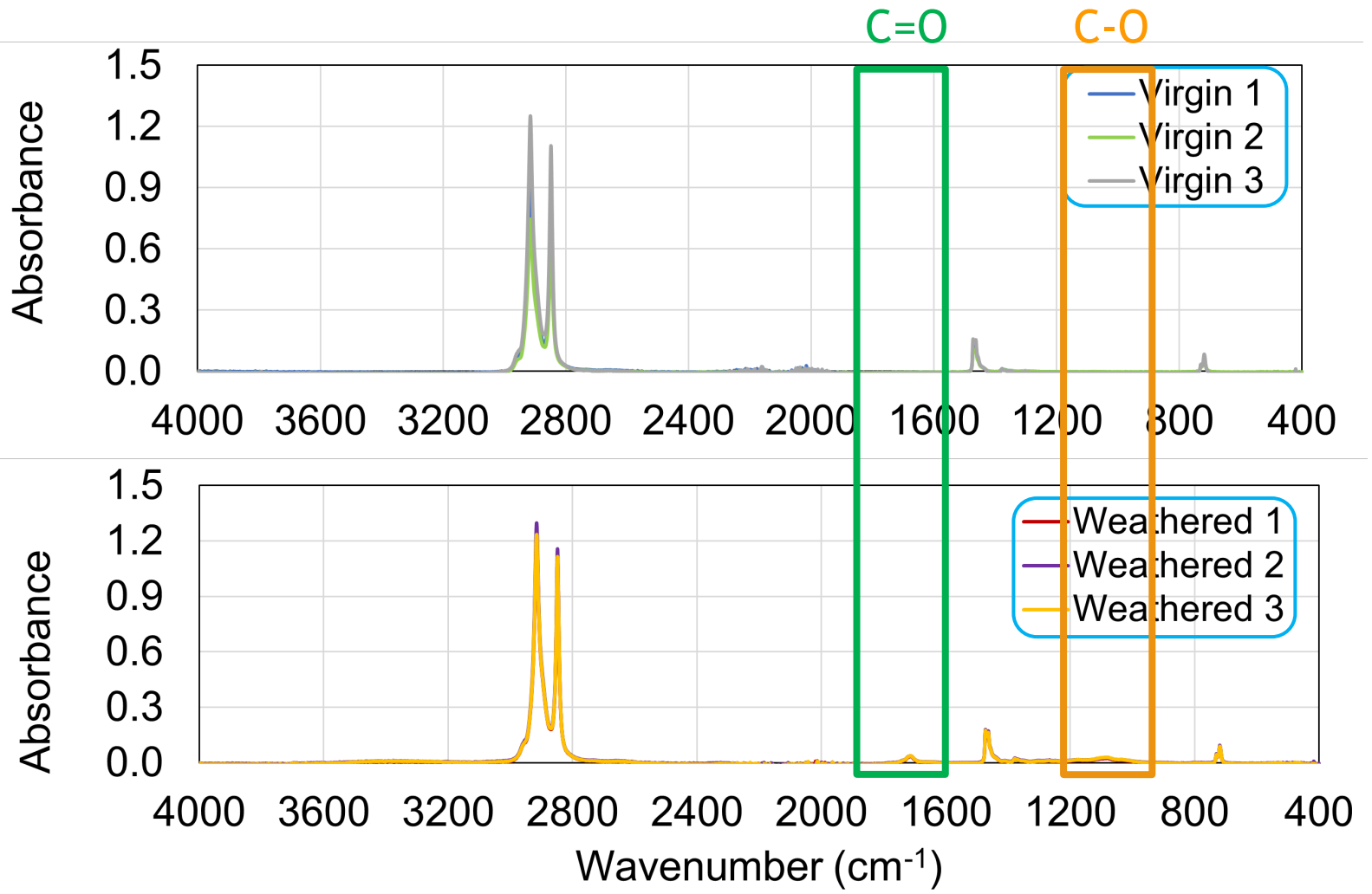
UV irradiation
- Artificial sunlight

Mechanical abrasion
- Sand
- Diffused air

Apply 8 weeks of artificial weathering to microplastics (*prior to use in trials*)



Impacts of Weathering: (FTIR spectra)



Observed increase in oxygen-containing groups

C=O: 1750-1690 cm^{-1}

C-O: 1140-940 cm^{-1}

Associated With:

Increased hydrophilicity ↑

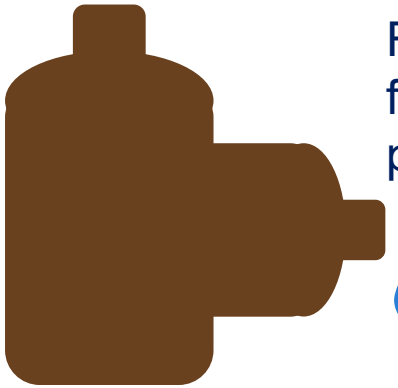
Increased crystallinity ↑

Potential decreased adsorption ↓

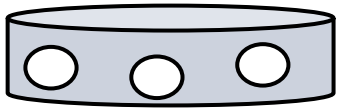
PFAS (& Microcystin) Adsorption Trials:

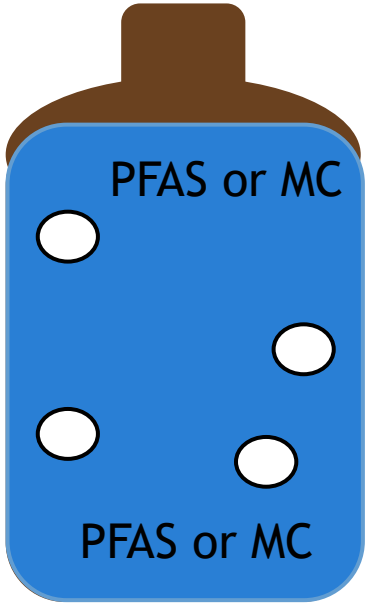
PFAS or Microcystins (MC)

Many different combinations of microplastic types & PFAS or Microcystin



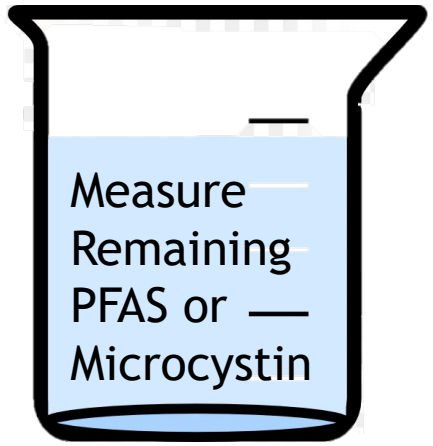
Filter/Syringe filter to remove plastics





250 mL for PFAS
20 ml for Microcystins

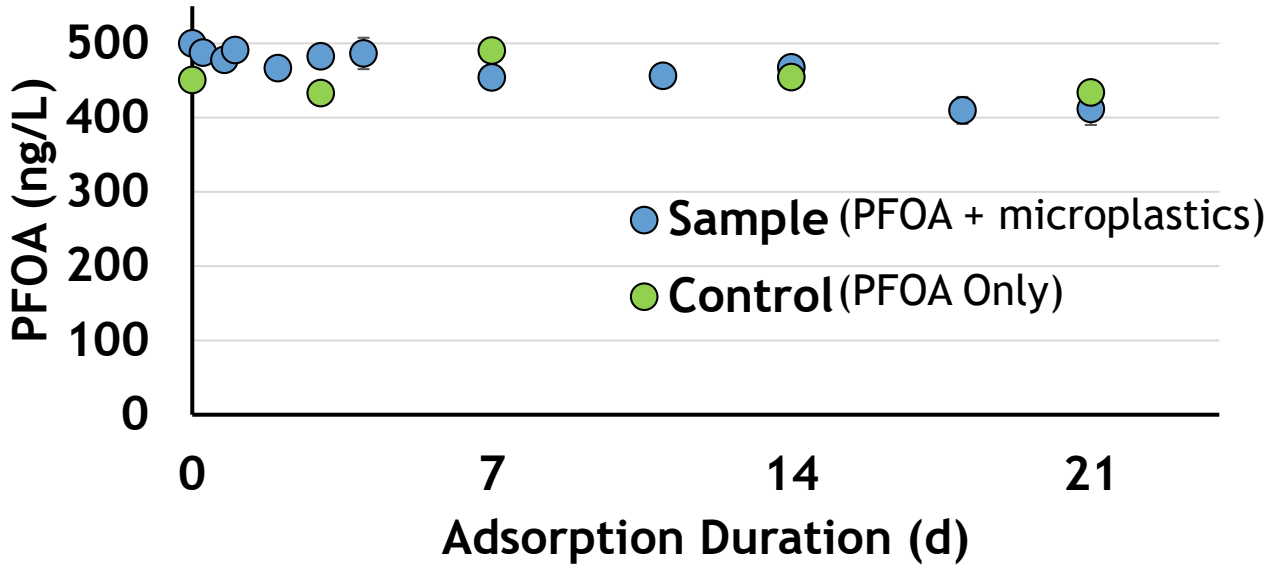
Mix microplastics (rotate end over end)



Initial PFAS Kinetics Trial (Using Virgin PE):

Assess:

1) Two sizes of Virgin PE: (200 µm & 1090 µm)
2) Time to reach equilibrium



No apparent impact of particle size

Adsorption levels off by 3 weeks

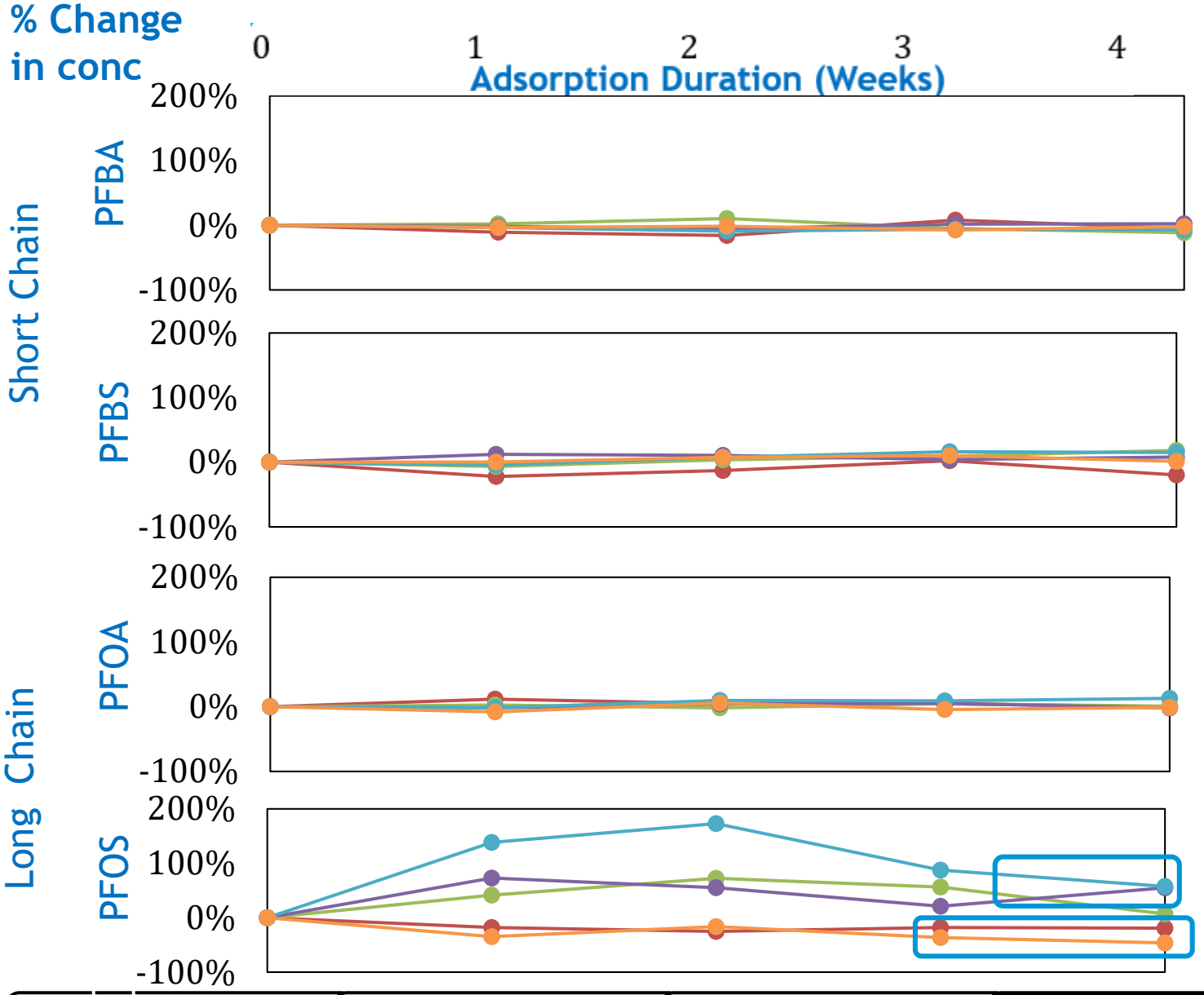
Subsequent PFAS Kinetic Trials (Using virgin PET, PS, PMMA,PVC):

Examine - 4 additional types of virgin microplastics (3,600 mg/L)

Polyethylene **T**erephthalate (PET)
Polystyrene (PS)
Poly(**m**ethyl **m**eth**a**crylate) (PMMA)
Polyvinyl **c**hloride (PVC)

Monitor remaining PFAS following 1, 2, 3, and 4 weeks

Calculate amount adsorbed (or leached)



Monitor PFAS Reduction

(conc. normalized to control samples)

Short Chain:

No significant changes observed

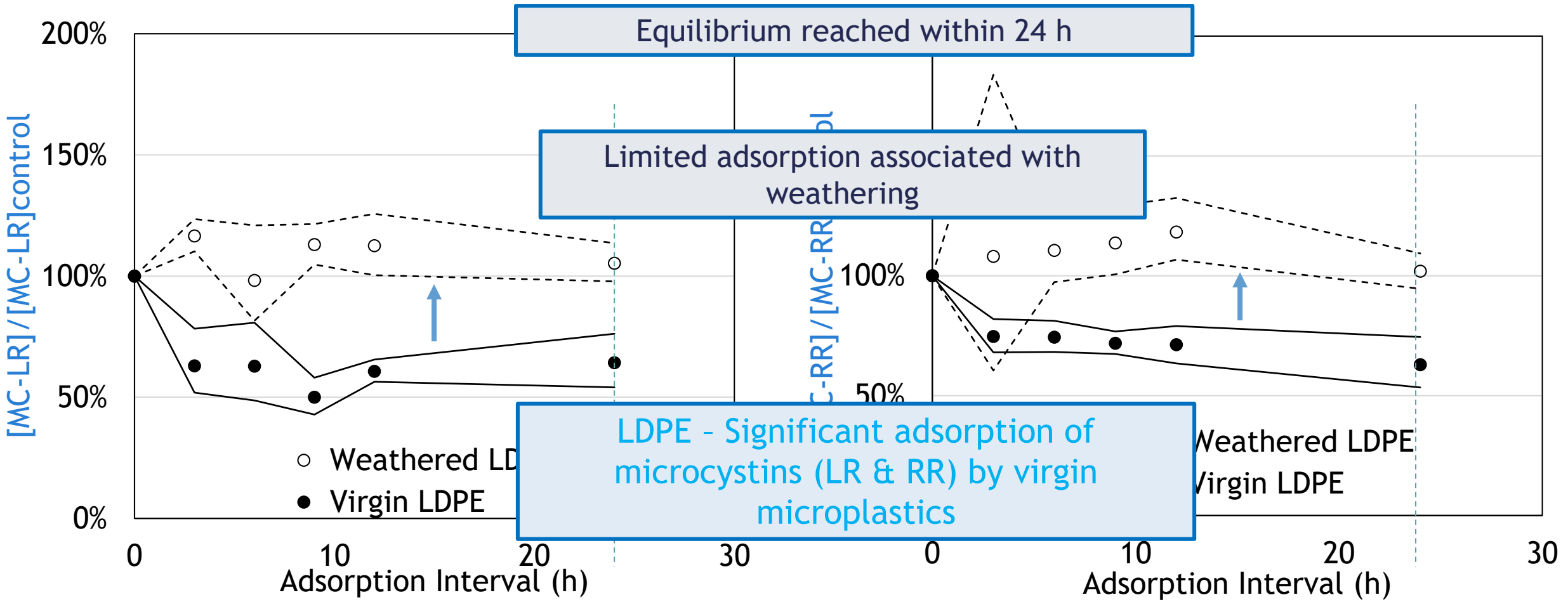
Long Chain:

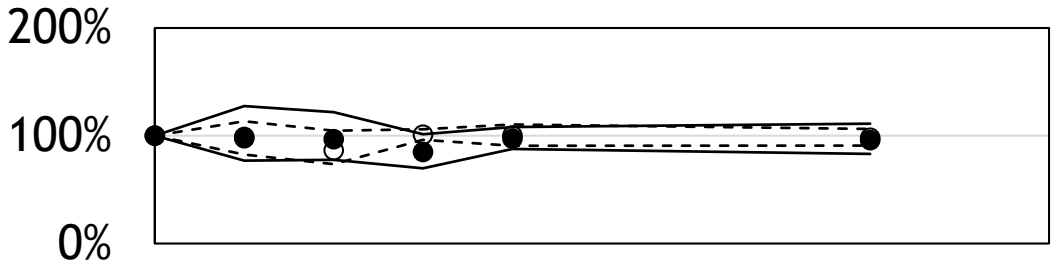
PFOS

Adsorption by PVC (50% loss),

Leaching from PS, PMMA

Microcystin Kinetic Trials (MCLR & MCRR) - LDPE:





Microcystin Trials (MCLR) for 4 additional polymer types (PET, PS, PMMA, PVC):

- No adsorption - by both virgin and weathered microplastics (for all 4 polymer types)
- Similar results for MCRR (not shown)

Summary:

1) Adsorption of PFOS by virgin PVC
   - Minimal adsorption for other PFAS and polymer types
   - Potential for leaching of PFAS by some polymer types
2) Adsorption of MC-LR and -RR by virgin LDPE
   - Minimal adsorption by other virgin polymer types, and all weathered polymers
3) Weathering associated with decrease in adsorption

Recommendations (for Future Research):

1) Examine additional source water matrices

(Do changes in water quality impact adsorption by microplastics?)

2) Employ naturally weathered microplastics

(Does impact of natural weathering differ when compared to in-lab artificial weathering?)

3) Employ small microplastics <20 µm in size

Primary Microplastics Funding:

Natural Sciences and Engineering Research Council (NSERC) - *Alliance Program*

Environment and Climate Change Canada (ECCC) - *Increasing Knowledge on Plastic Pollution Initiative*

+ Municipal & Industry Partners:

City of Barrie
Durham Region
Eugene Water & Electric Board
Lake Huron and Elgin Area Primary Water Supply Systems (London)
Peterborough Utilities Commission
Ontario Clean Water Agency
Regional Municipality of York
Regional Municipality of Peel
Toronto Water
Brown & Caldwell

Questions?

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