Producing secondary nano- and microplastics by photooxidation and (or) mechanical abrasion

Microplastics in the World Ocean
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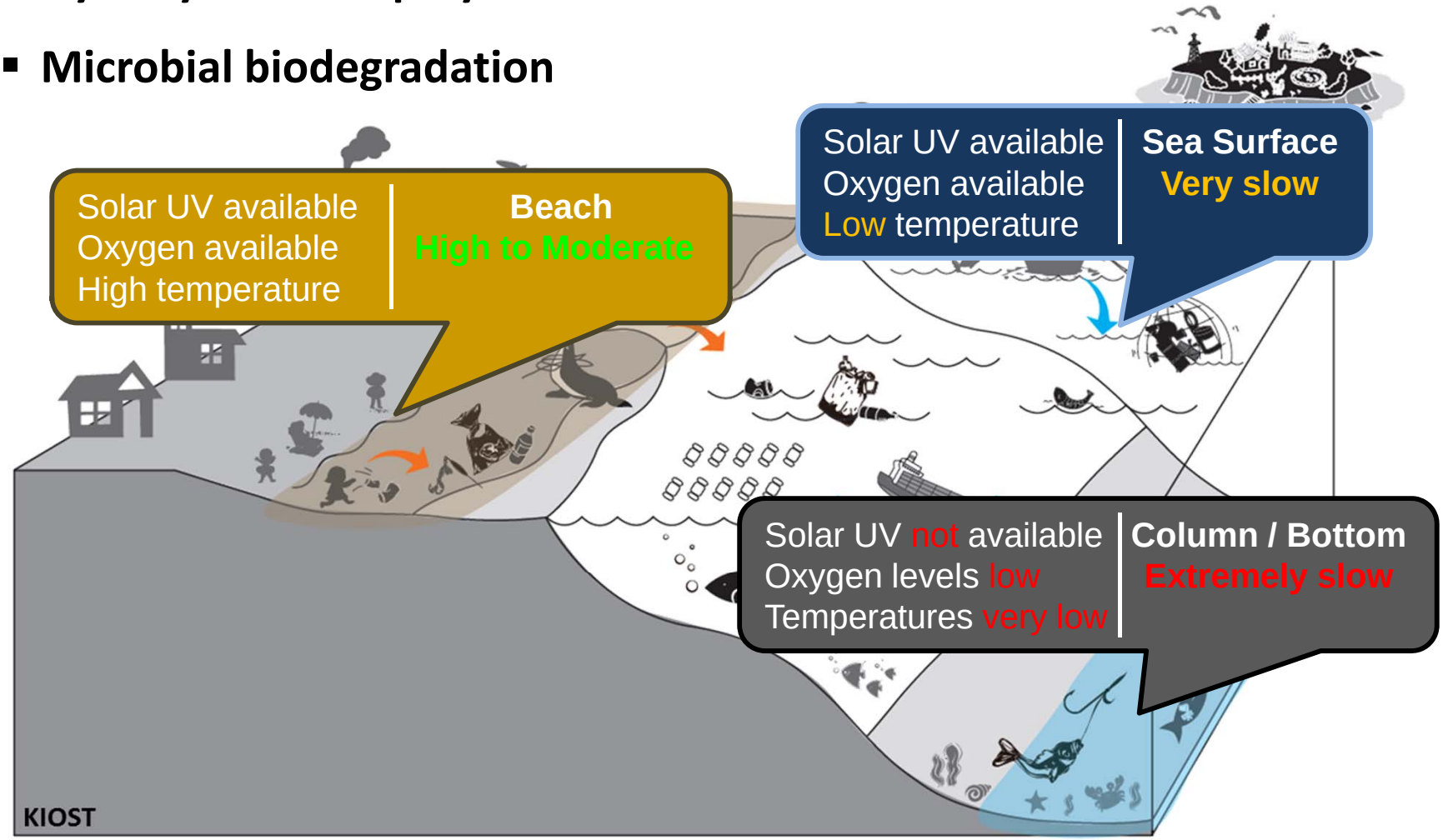
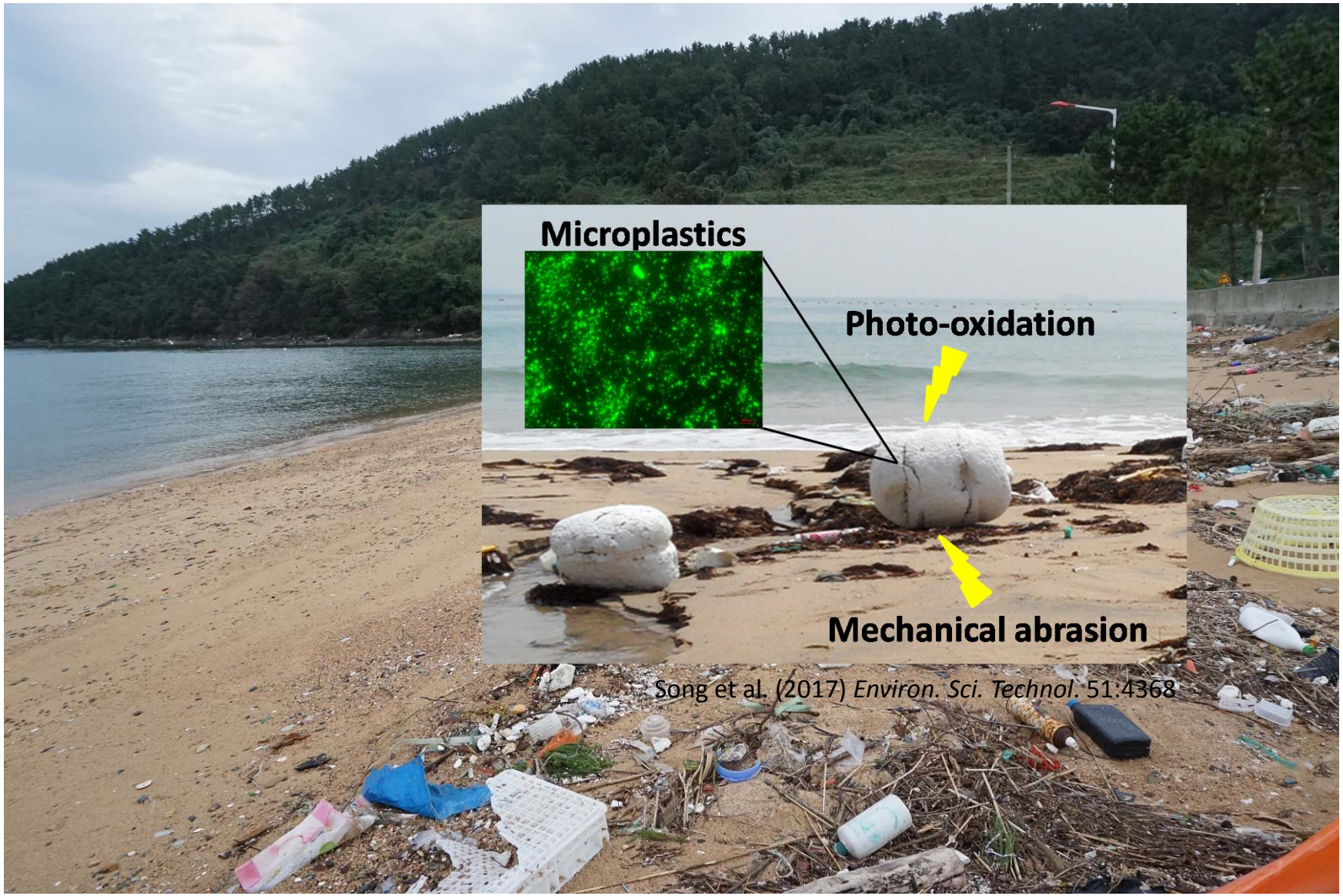
Weathering of plastics in the environment

- **Solar UV-induced photochemical oxidation**
- **Thermal reactions including thermal oxidation**
- **Hydrolysis of the polymer**
- **Microbial biodegradation**



Weathering of plastics on the beach environment

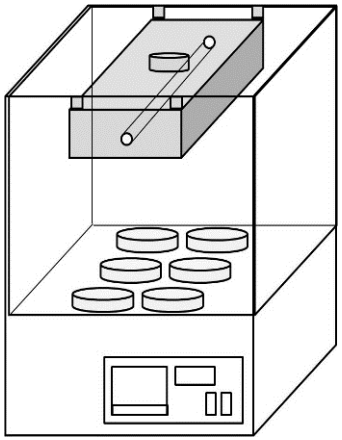
How many nano- and microplastics are generated by natural weathering?

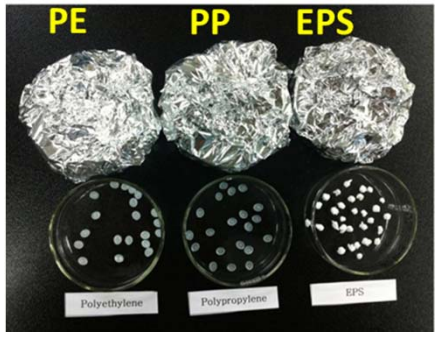


Song et al. (2017) *Environ. Sci. Technol.* 51:4368

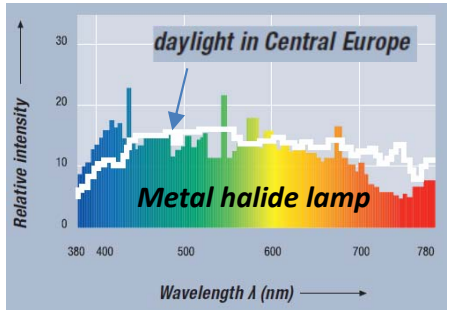
Accelerated fragmentation exp. : UV exposure + mechanical abrasion

UV exposure



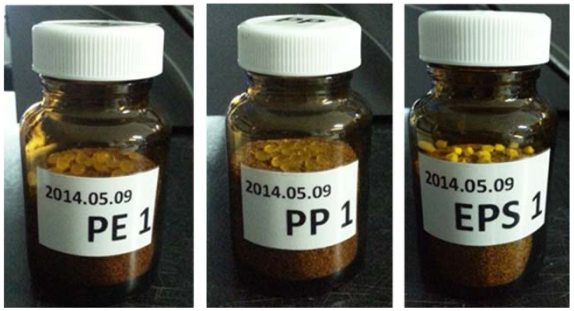


- Low Density Polyethylene (LDPE), Polypropylene (PP), Expanded polystyrene (EPS)
- Temp: 43-45℃
- Period: 2, 6 & 12 months
- UV: Metal halide lamp



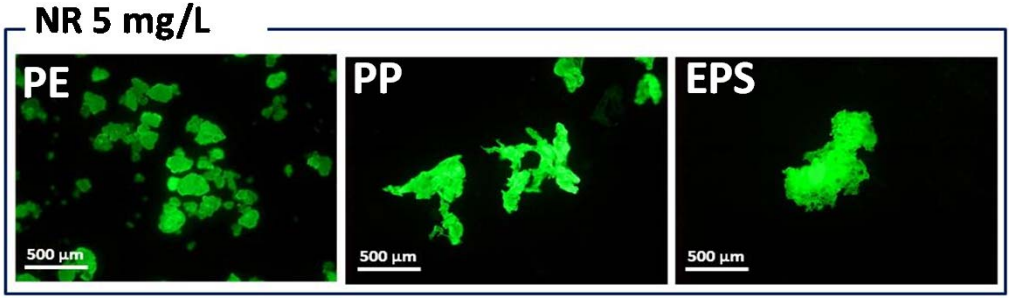
Mechanical abrasion

- Rolling with sand at about 36-38 rpm
- Period: 2 months
- Triplicates

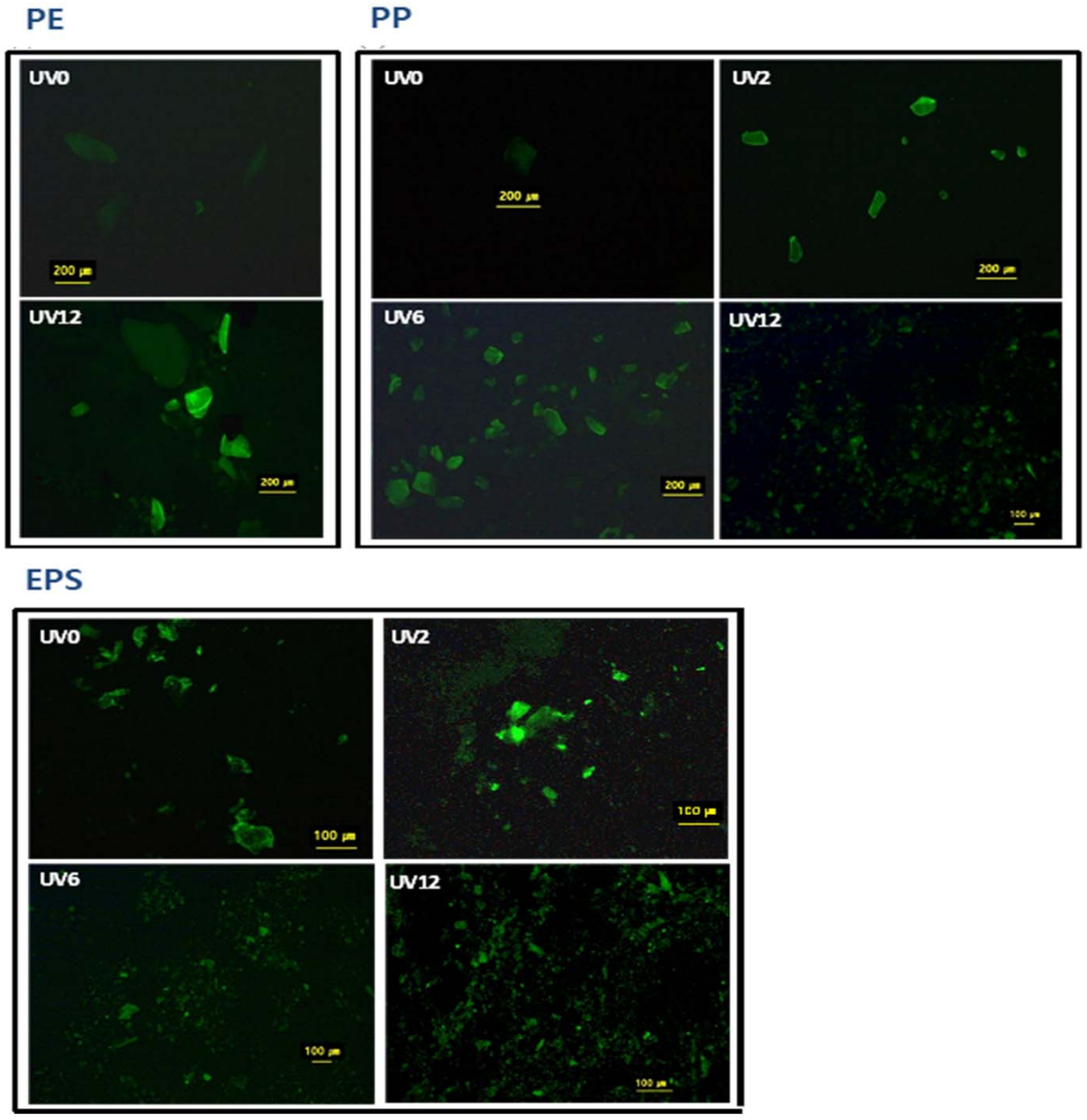


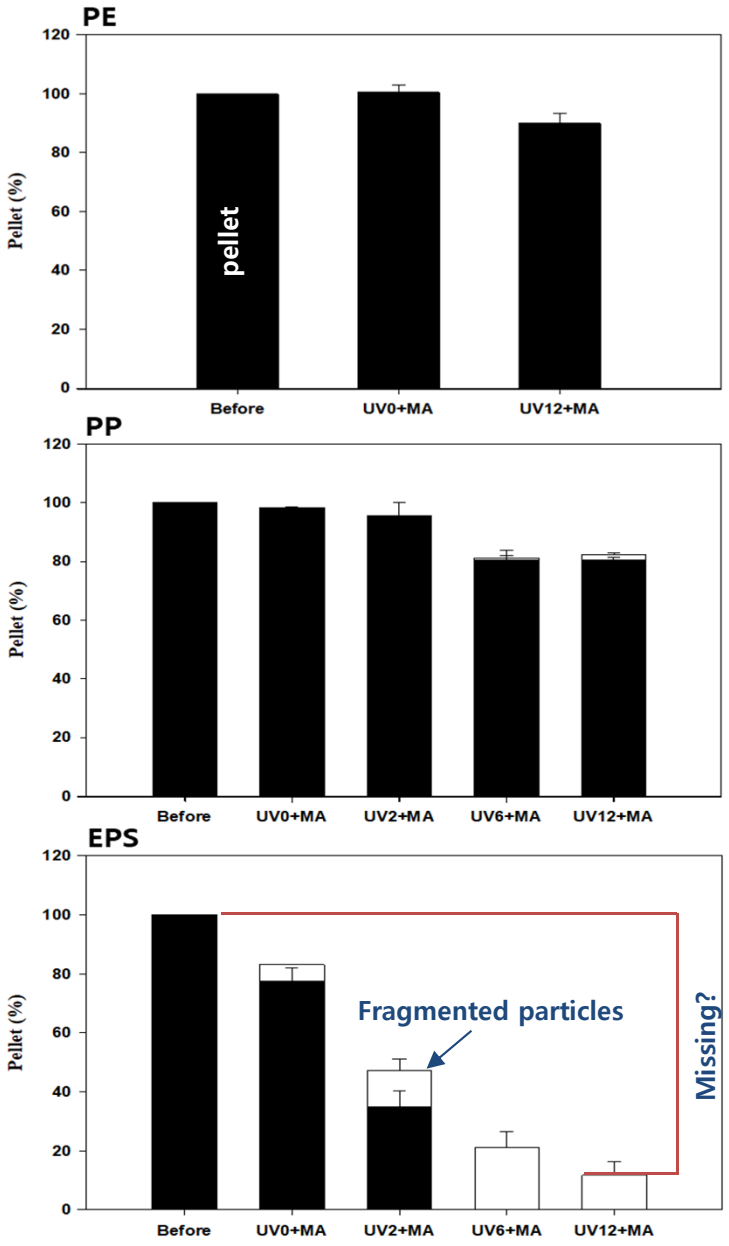
Nile Red staining

- Staining on a filter paper with 200 µl of 5 mg/L Nile Red solution in hexane
- Washing with 100 µl of hexane
- Quantification with a fluorescent microscope (~ x200)
- Ex/Em wavelength: 450-490 / 515-565 nm



Fragmentation of microplastics by UV exposure and subsequent mechanical abrasion (MA) with sands

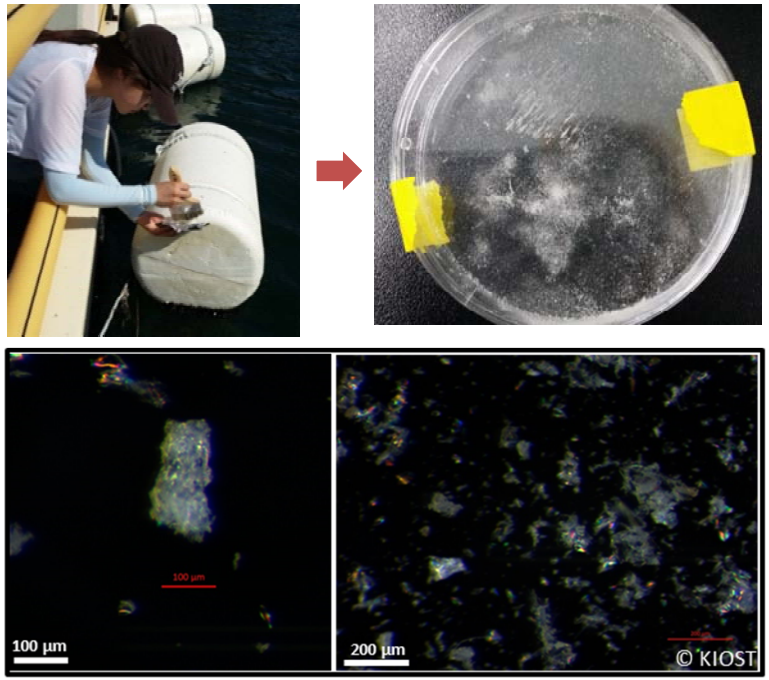




Song et al. (2017) *Environ. Sci. Technol*. 51:4368

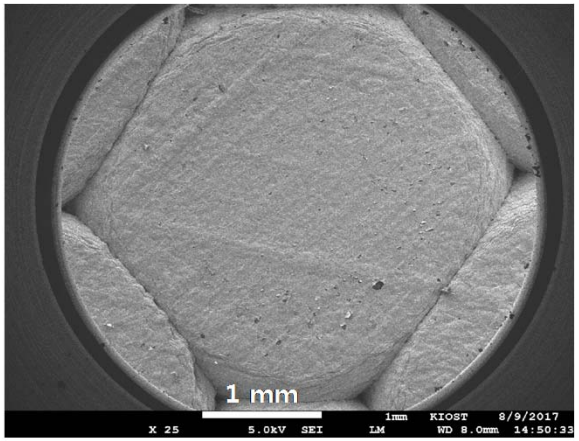
Why expanded polystyrene (EPS)

- **Common litter item and widespread in marine and fresh water**
  - Reddy et al., 2006, Corcoran et al., 2015, Collignon et al., 2012, Poeta et al., 2014, Kang et al., 2015
- **Identified as being exceptionally high in abundance on beaches mostly in Asia**
  - Lee et al., 2013, Heo et al., 2013, Fok and Cheung 2015, Fok et al., 2017, Hinojosa and Thiel, 2009, Vietnam (GreenHub)
- **Large amount of EPS floats have been used in aquaculture in Asian countries**
- **Susceptible to outdoor weathering and easily fragmented by UV exposure**

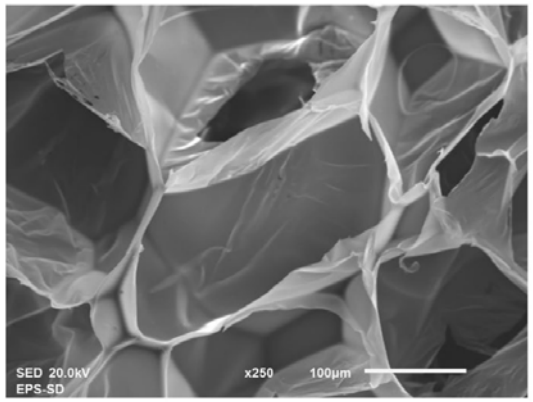


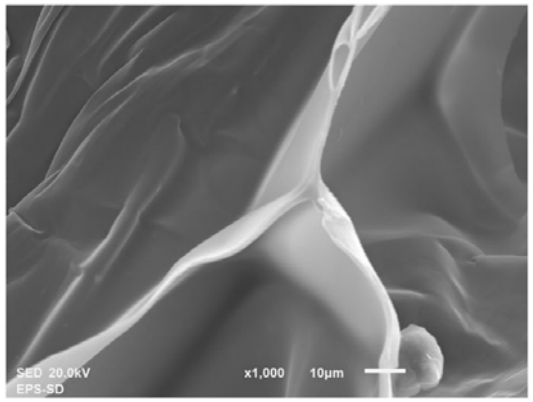
Foamed structure of EPS

Interior of new EPS

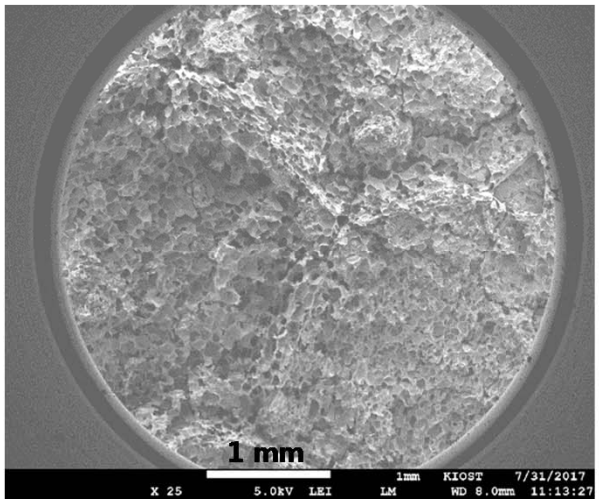


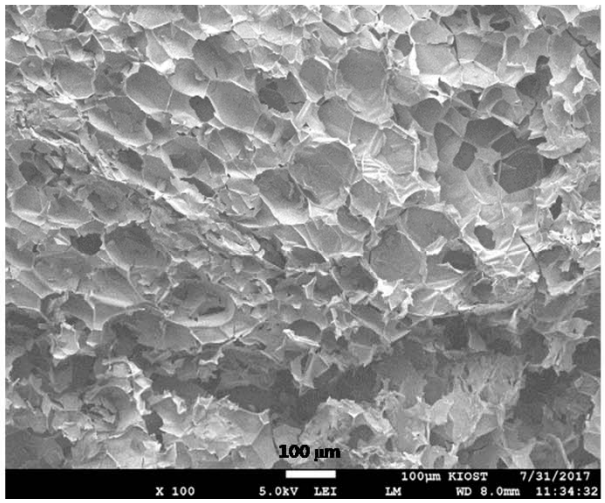
Mejia-Torres et al. (2018) *Polym. Bull*. 75:5619

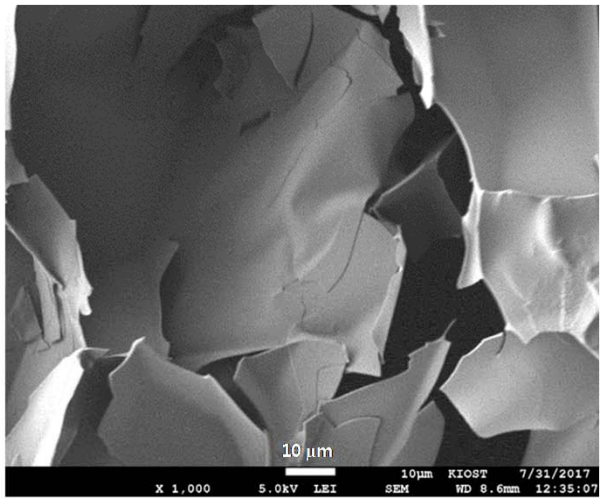




Interior of weathered EPS for 9 months

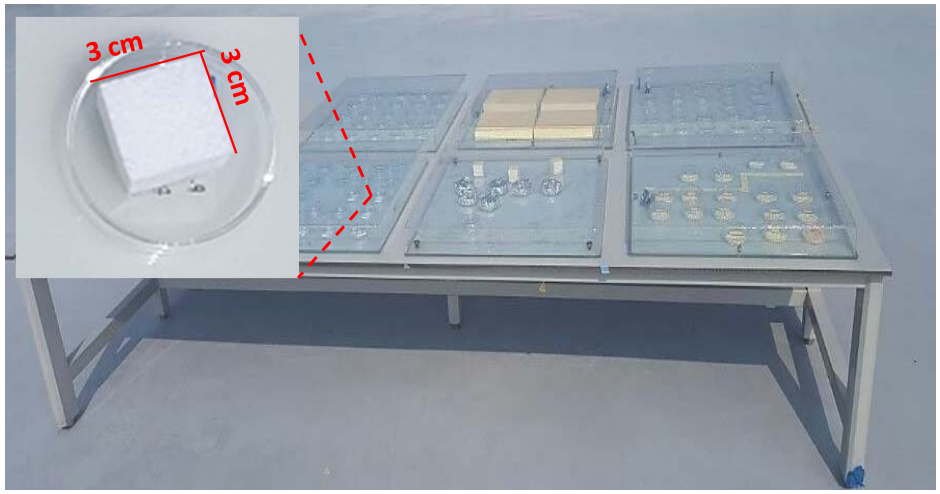






Fragmentation by sunlight exposure

Sunlight exposure

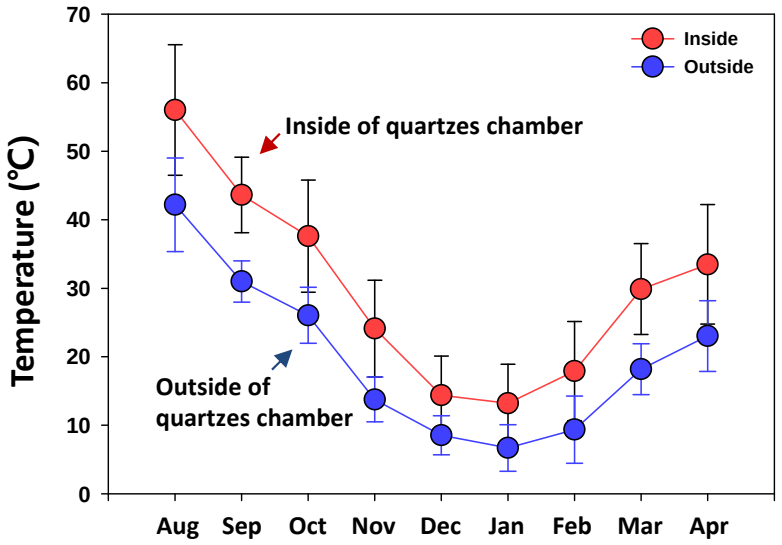


- Polymer: EPS container purchased from a market
- EPS cube: placed in borosilicate Petri-dish w/o lid
- Quartzes chamber: 50 x 50 cm
- Exposed top surface area: 3 x 3 cm
- Sunlight exposure duration: ~24 months
- Subsample: 3, 6, 7, 9, and 24 months
- Place: KIOST, Geoje, South Korea

Total solar irradiance and temperature

- 3 Mon (3M) : 1.0 (1,641 MJ/m^2)
- 6 Mon (6M) : 1.4 (2,352 MJ/m^2)
- 7 Mon (7M) : 1.6 (2,632 MJ/m^2)
- 9 Mon (9M) : 2.4 (3,995 MJ/m^2)
- 24 Mon (24M): 7.6 (12,391 MJ/m^2)

- Based on average total solar irradiance measured per hour in 2009-2010 in Geoje, South Korea



- Geoje, South Korea

Additive chemicals in EPS

LC-MS/MS (HPLC-TQ5500)

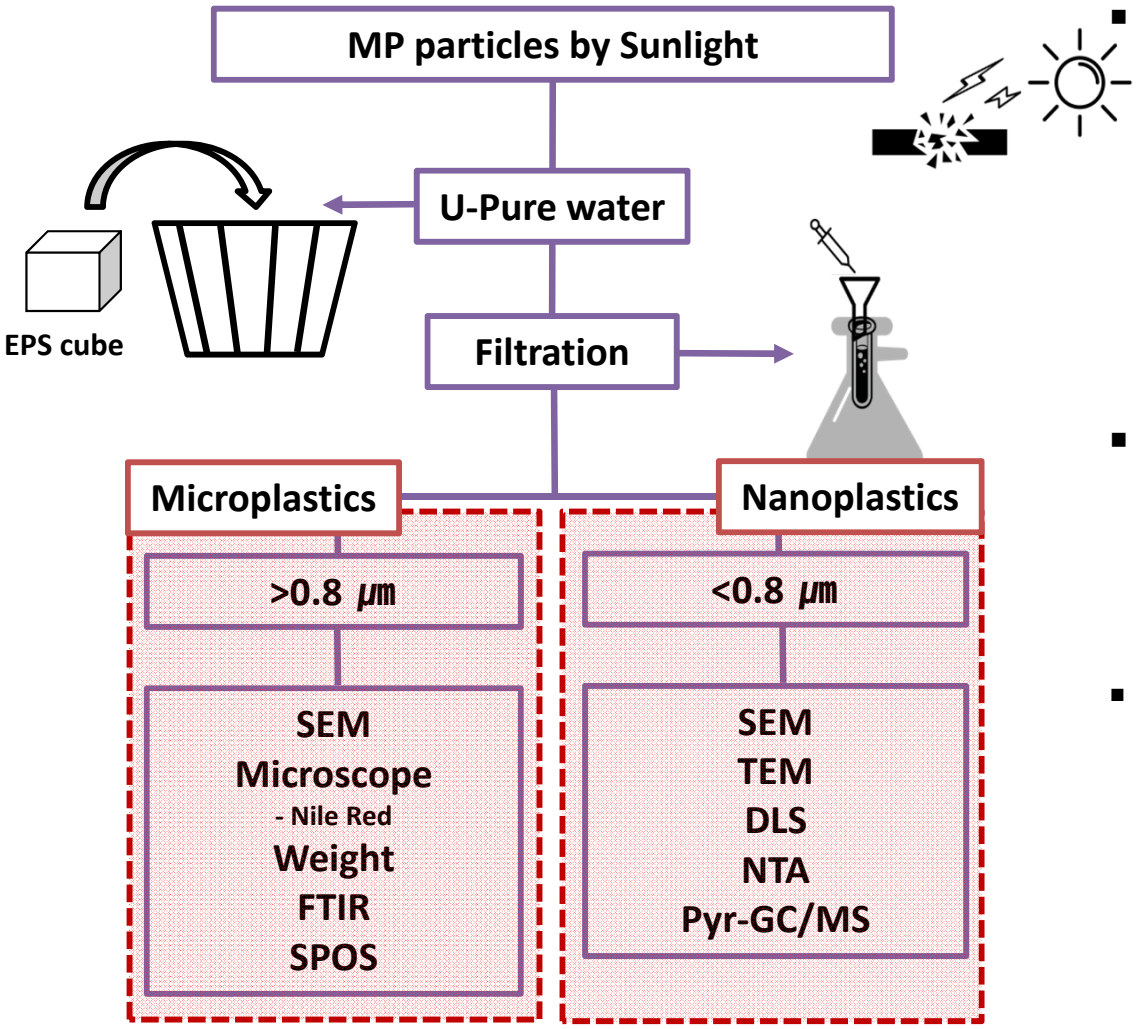
Unit: ng/g

Additive chemicals		EPS #1	EPS #2
Plasticizer	DBP	1,157	787
	DnOP	N.D	N.D
UV stabilizer	UVMC80	N.D	N.D
	UV320	N.D	N.D
	UV326	N.D	N.D
	UV327	N.D	N.D
	UV328	N.D	N.D
Antioxidant	2,4-DTBP	N.D	N.D
	Irganox 1010	N.D	N.D
	Irganox 1076	N.D	N.D
Surfactant	NP	N.D	N.D
Bisphenol-A	BPA	N.D	N.D
Brominated Flame Retardants	α-HBCD	78,840	72,866
	β-HBCD	105,120	117,988
	γ-HBCD	78,499	85,366
	PBCD	354,949	393,293

*N.D: Not Detected

Recovery and analysis of the fragmented particles

Particle analysis



- Two different groups according to size

  >0.8 μm (micro)/ <0.8 μm (nano)

- Image and qualitative analysis

  - Scanning electron microscope-energy dispersive spectroscopy (SEM-EDS)
  - Fluorescence microscope
  - Transmission electron microscopy (TEM)

- Average size

  - Nanoparticle tracking analysis (NTA)

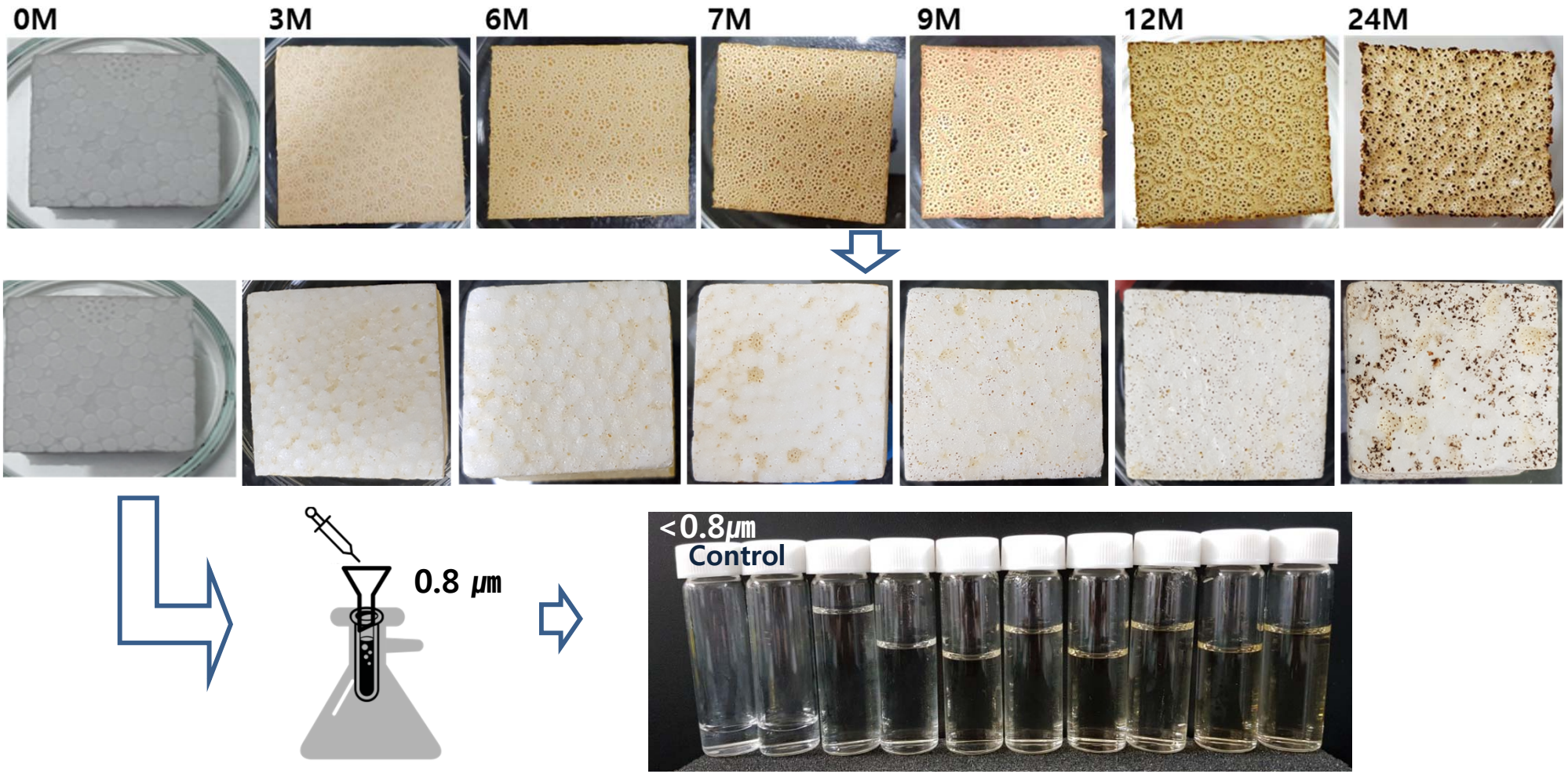
    (NTA; viewsizer300): 10 nm-2 μm

- Particle size distribution & concentration

  - NTA: 10 nm-2 μm
  - Single particle optical sizing (SPOS): 0.5-2500 μm

Exposed surface change and recovery of the fragmented particles

After sunlight exposure



1. Soaking the top surface in the 2 ml of solution (ultra pure water) in aluminum dish
2. Filter the solution with 0.8 μm PC filter
3. Weighing the particles on 0.8 μm filter

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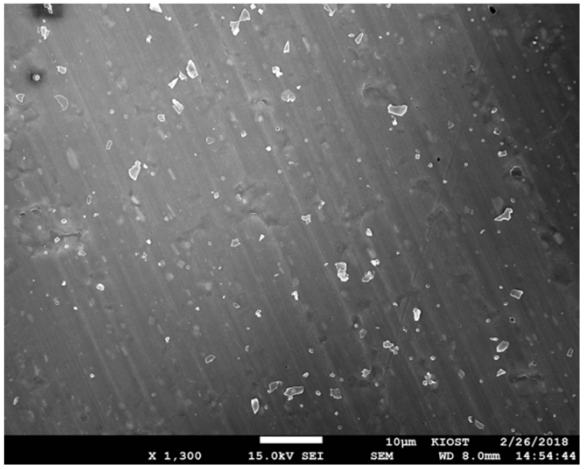
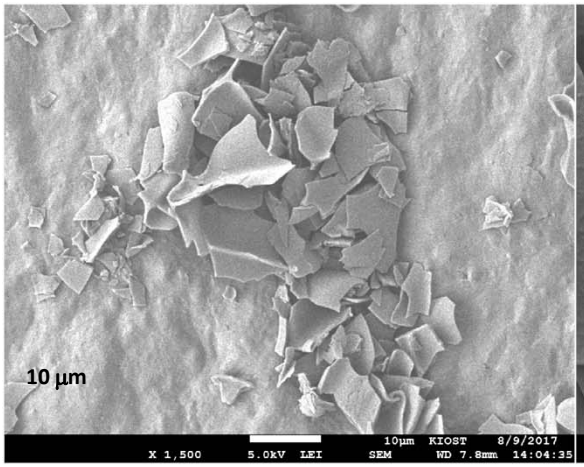
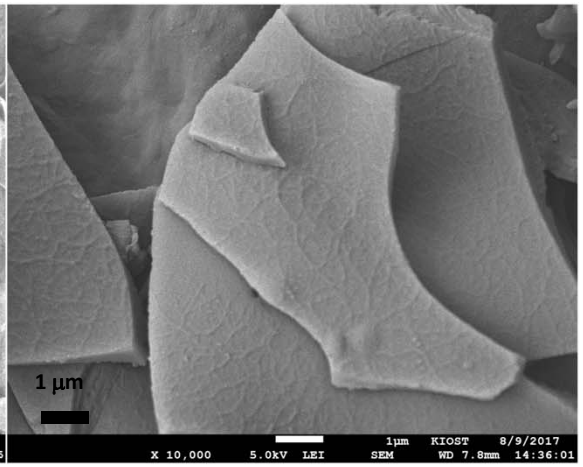
Qualitative analysis of the produced microplastics

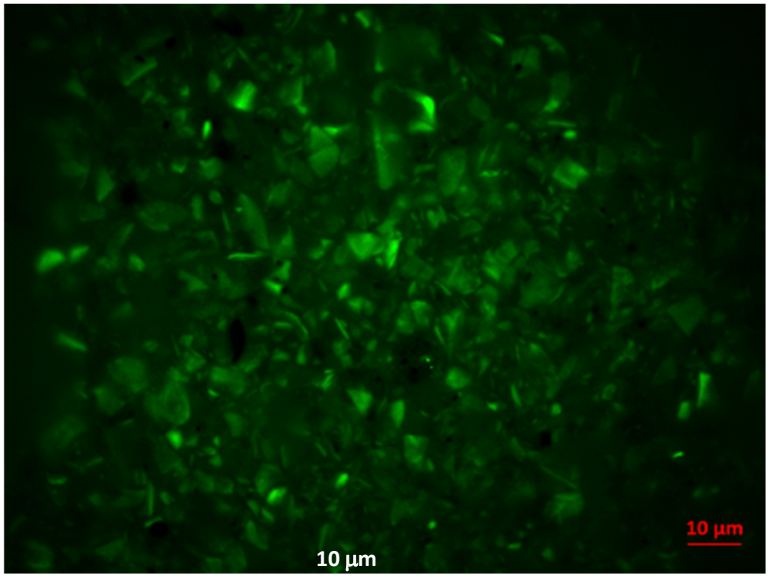
Micro-sized particles (>0.8 μm)

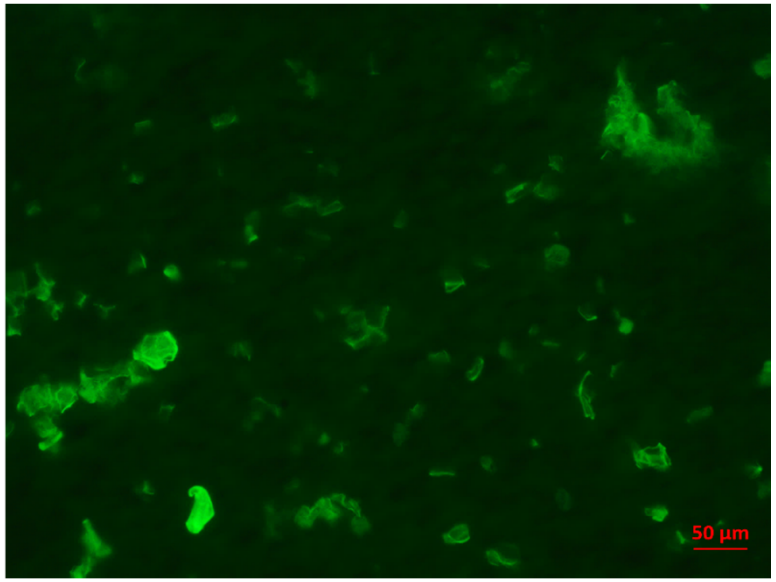






Nile Red staining





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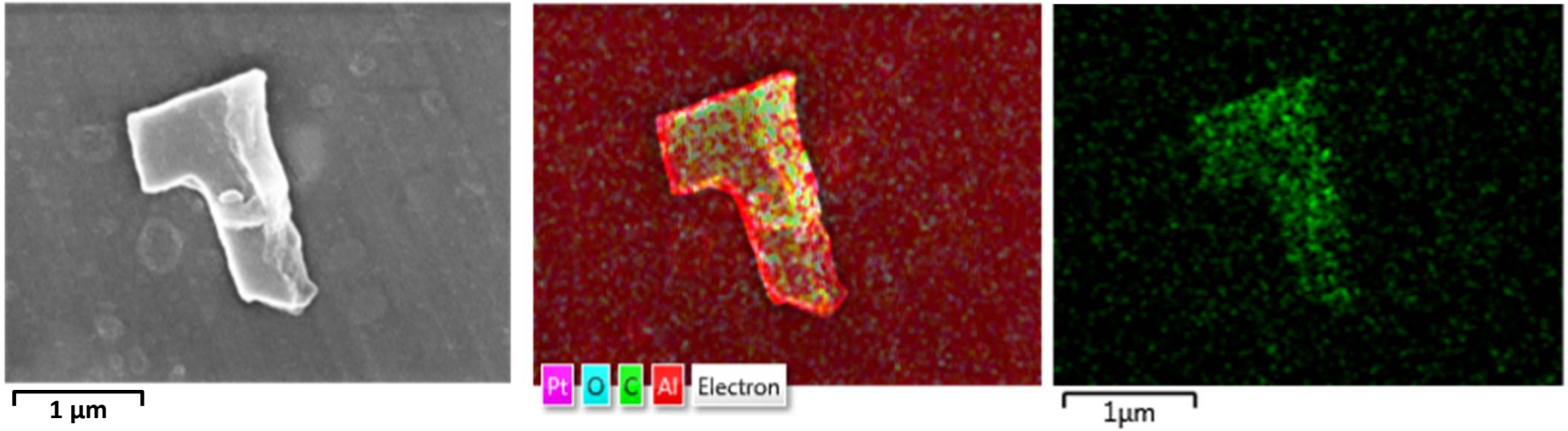
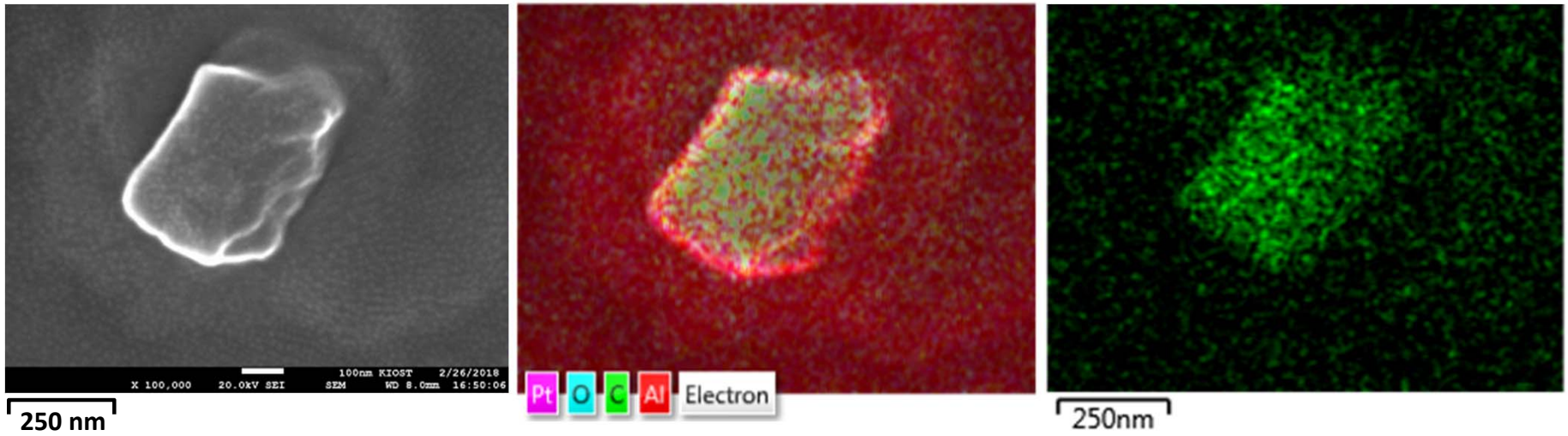
Qualitative analysis of the produced micro- and nanoplastics: SEM-EDS

Microplastics (>0.8 μm)



Nanoplastics (<0.8 μm)



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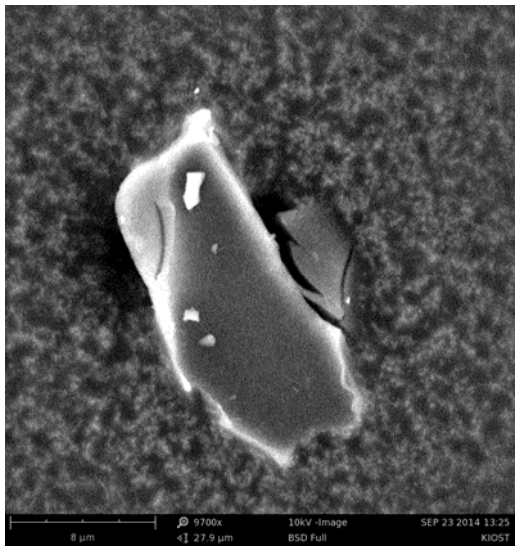
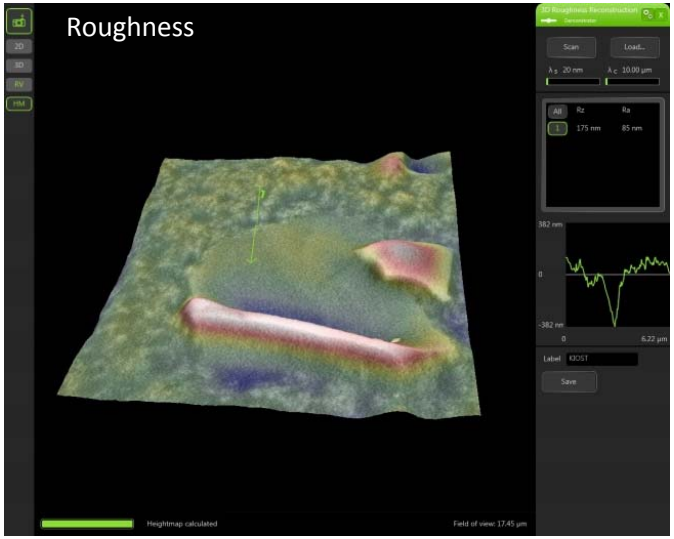
Qualitative analysis of the produced micro- and nanoplastics: TEM

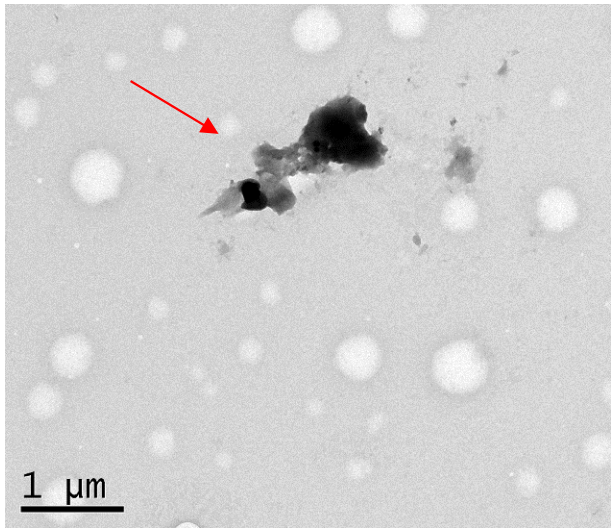
Microplastics (>0.8 μm)

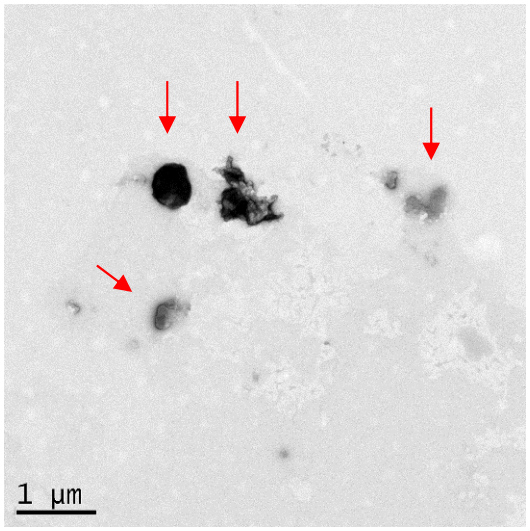


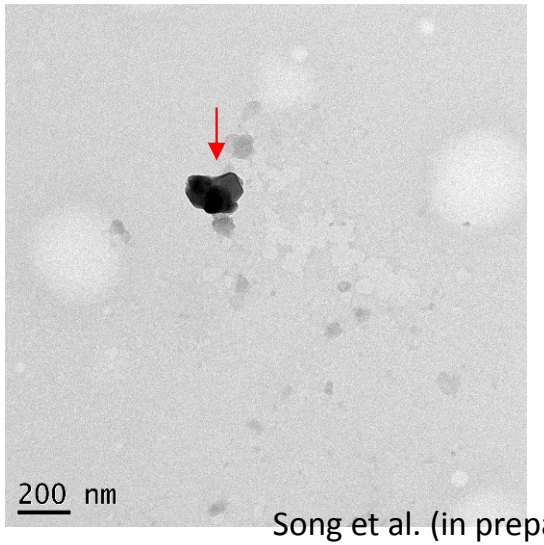


- ✓**Size: 10-20 µm**
- ✓**Surface roughness:**
  - **Rz: 175 nm**
  - **Ra: 85 nm**

Nanoplastics (<0.8 μm)







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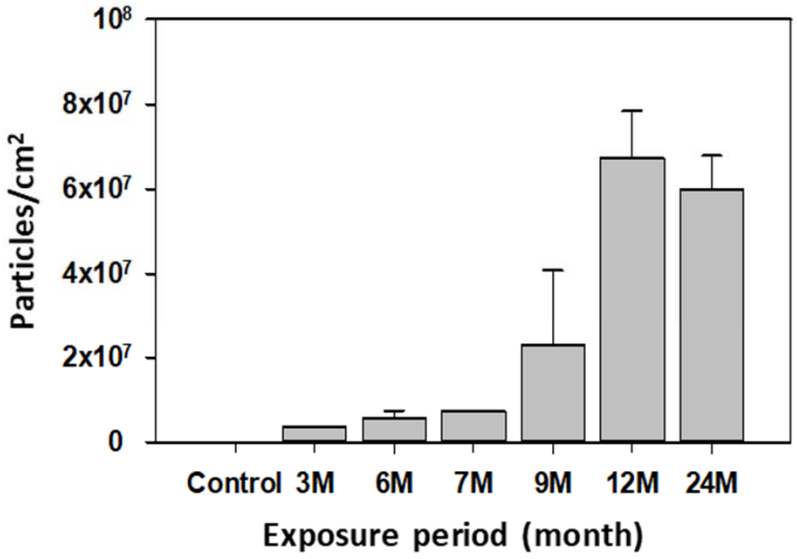
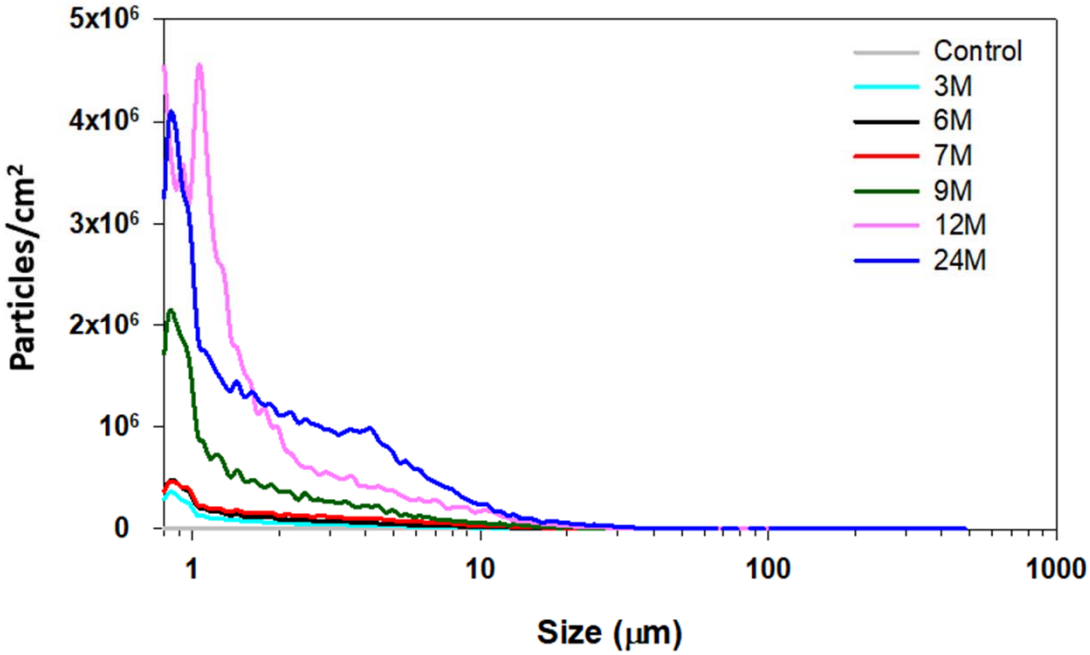
Produced microplastics and particle size distribution (>0.8 μm)

Produced particles



Particle size distribution



Average size

Sample	Average size (μm)
3M	2.32
6M	2.32
7M	2.88
9M	2.20
12M	2.03
24M	2.78

- Approximately, **3.7x10⁶-6.7x10⁷ particles/cm²** were produced.
- Increasing particles by increasing exposure duration
- A comparable average size of fragmented particles

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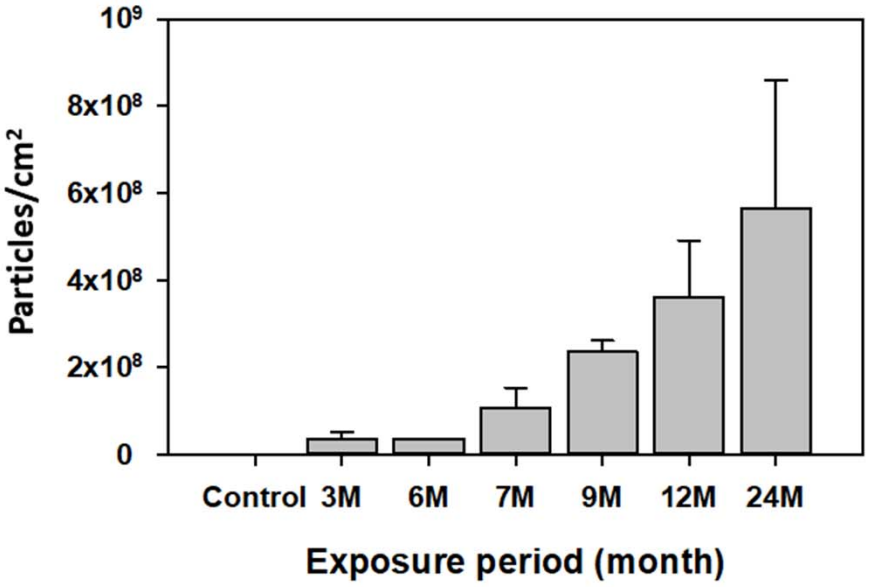
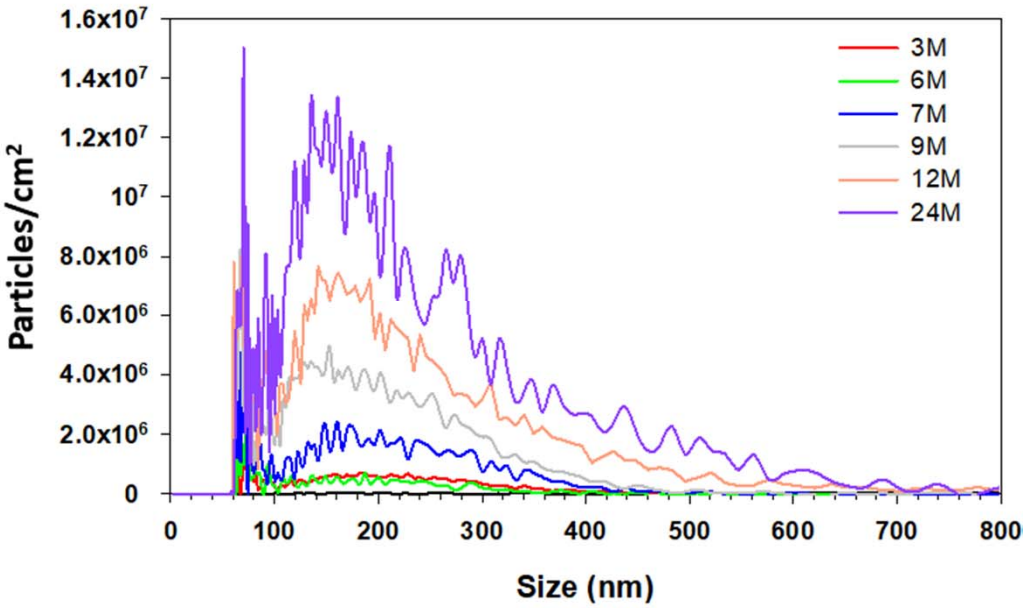
Produced nanoplastics and particle size distribution (<0.8 μm)

Produced particles



Particle size distribution



Average size

Sample	Average size(nm)
3M	138
6M	145
7M	164
9M	159
12M	178
24M	189

- **Approximately, $4x10^7$-$5x10^8$ particles/cm^2 were produced.**
- **Increasing particles by increasing exposure period**
- **A comparable average size of fragmented particles**

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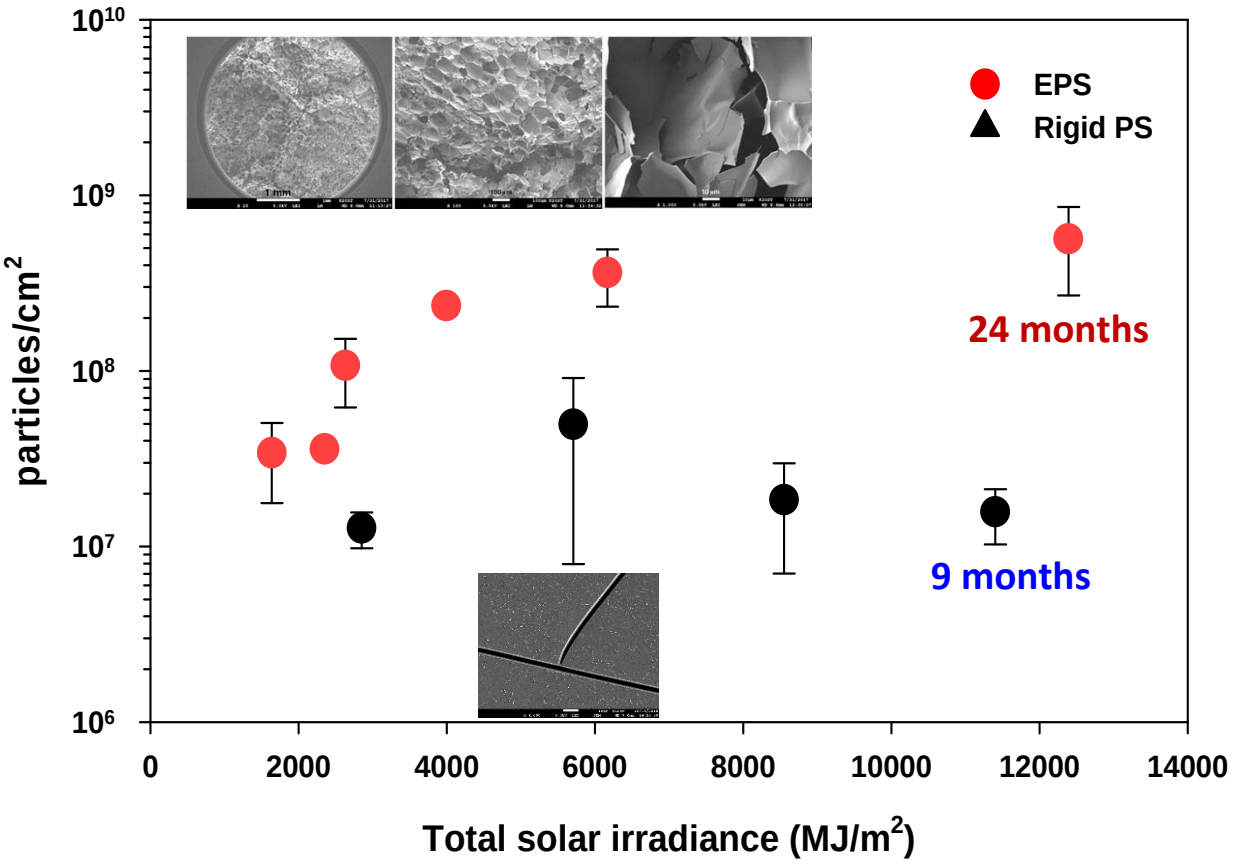
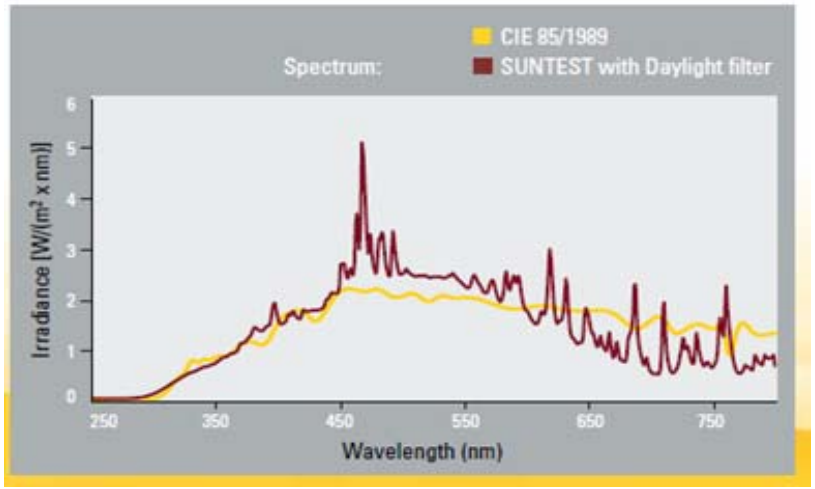
EPS *vs* rigid PS in nanoplastic production

EPS (sunlight exposure) vs rigid PS (simulating sunlight exposure)



<Suntest XLS+(left) and rigid polystyrene sample placed on galvanized steel plate for UV exposure (right)>



<Global Solar Irradiance at sea level (yellow) and Suntest with Daylight filter (red)>

- **Rigid PS: 3x5 cm sheet**
- **Suntest XLS+: Xenon lamp/Daylight filter, cut-on at approx. 295 nm**
- **Exposure duration: 2, 4, 6 and 8 months**

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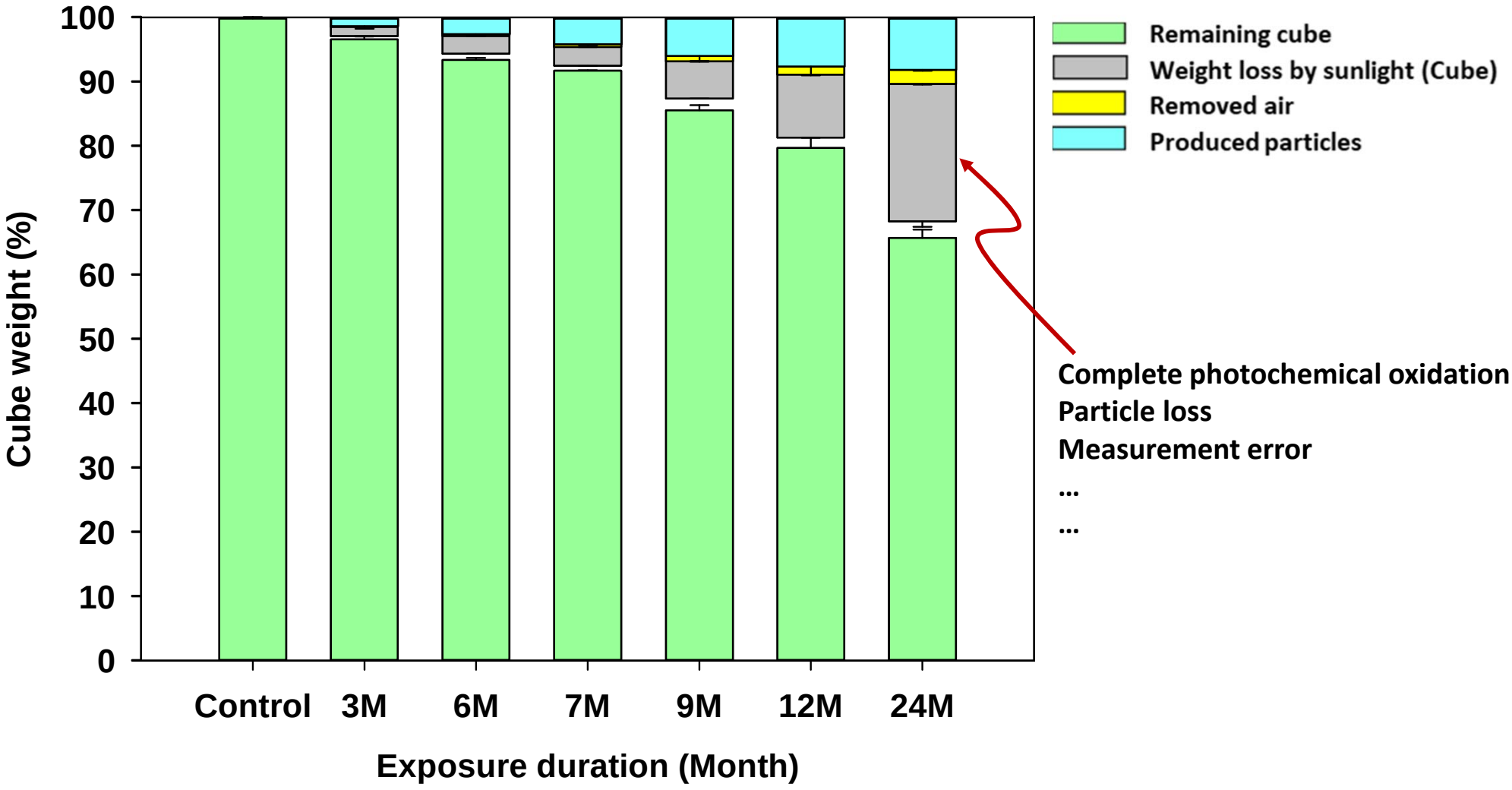
Mass balance of EPS exposed to sunlight

Weight loss of EPS cube



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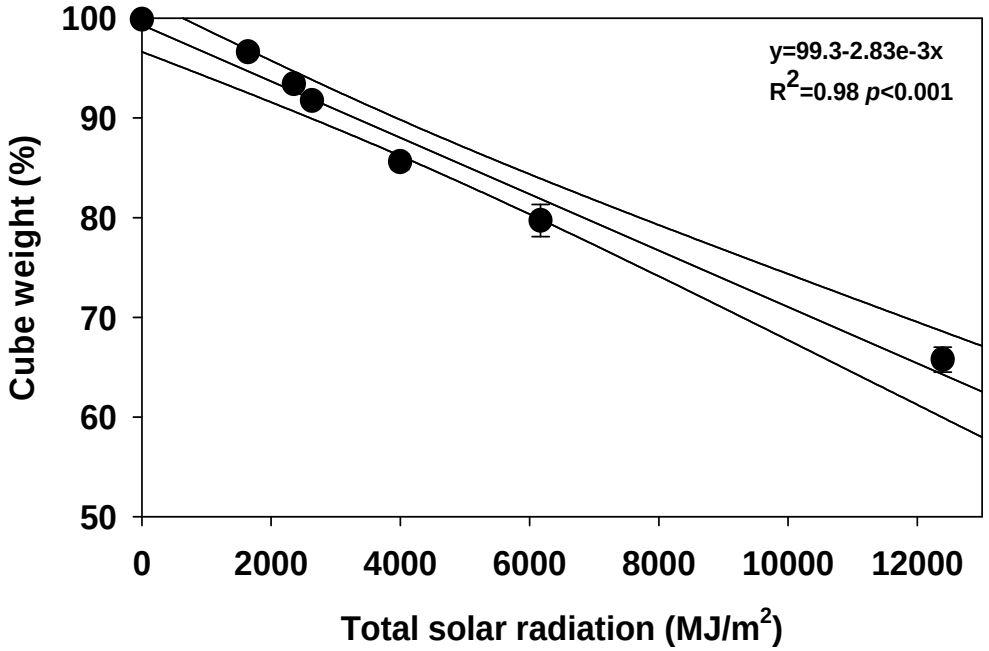
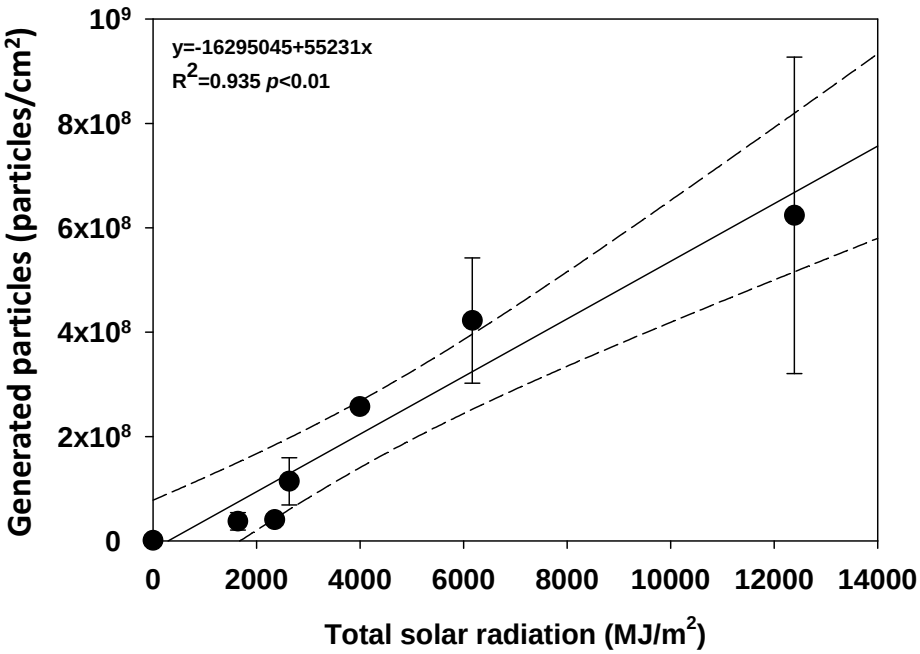
Estimation of nano- and microplastic production rate

EPS cube weight of loss



Generated micro & nano particles



- It requires approximately 3.5 years to lose 50% of EPS cube based on the estimated weathering rate.

- Approximately 2.6×10^8 particles/cm^2 can be produced for 1 year (4,998 Mj/cm^2) .

- The estimated NMP production rate
  - 2.2×10^8 particles/cm^2·yr (0.13 μg/cm^2·yr) for nanoplastics
  - 4.2×10^7 particles/cm^2·yr (670 μg/cm^2·yr) for microplastics

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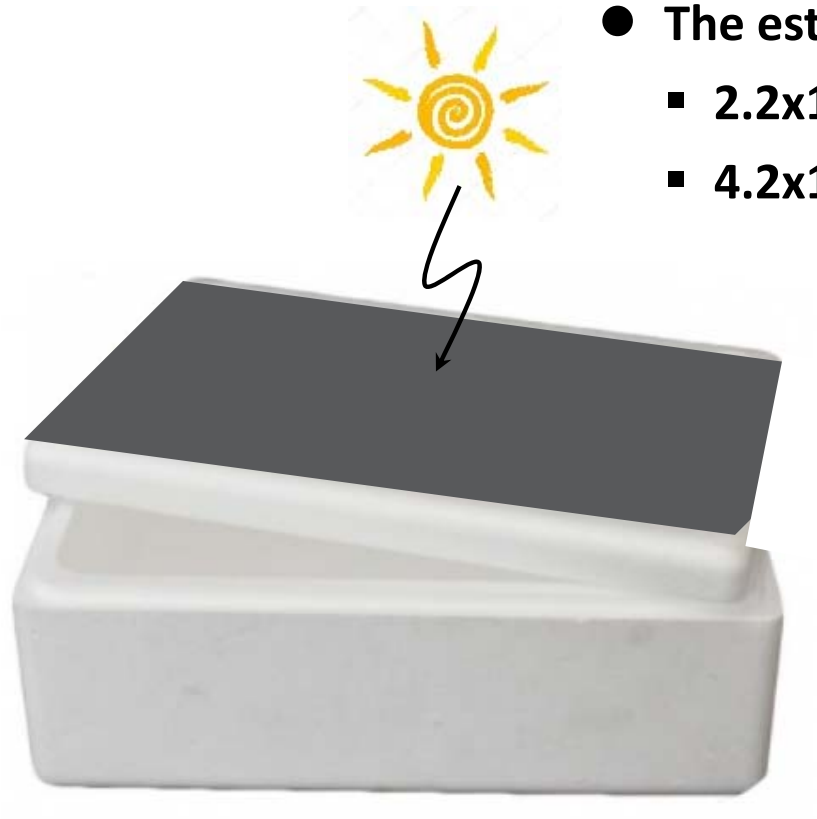
Generation of nano- and microplastics from EPS exposed to sunlight

Generated nano- and microplastics from the top surface area of EPS container



- **The estimated production rate**
  - **2.2×10^8 particles/cm^2·yr (0.13 μg/cm^2·yr) for nanoplastics**
  - **4.2×10^7 particles/cm^2·yr (670 μg/cm^2·yr) for microplastics**

- ✓ **Surface area: 30 x 40 cm**
- ✓ **1200 cm^2 x NMP production rate**

  = 2.6×10^{11} nanoparticles/yr (0.16 mg/yr)

  +5.0×10^{10} microparticles/yr (804 mg/yr)

  = 3.1×10^{11} PS particles/yr

  or

  0.8 g PS/yr

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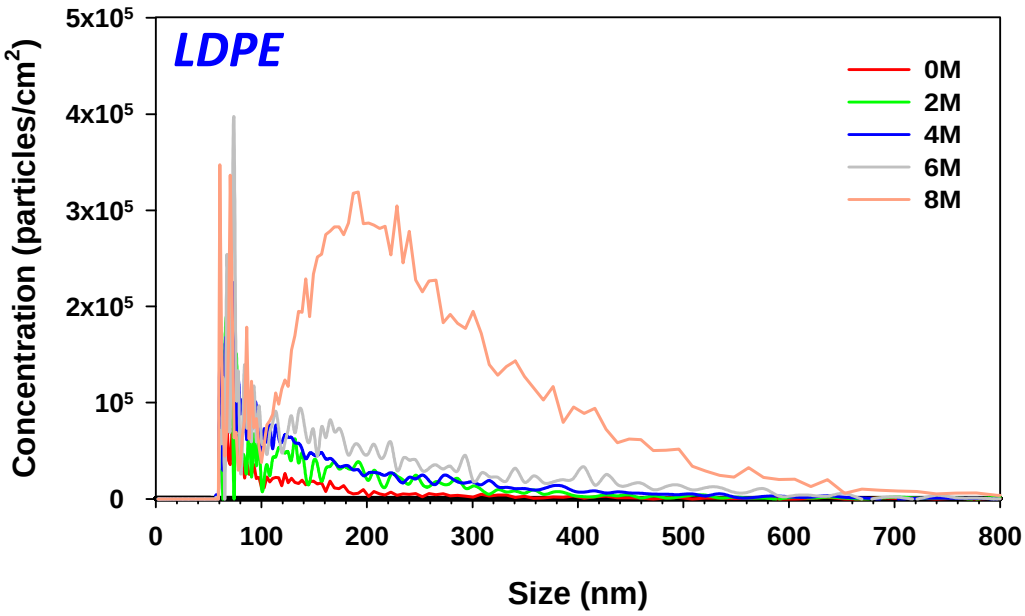
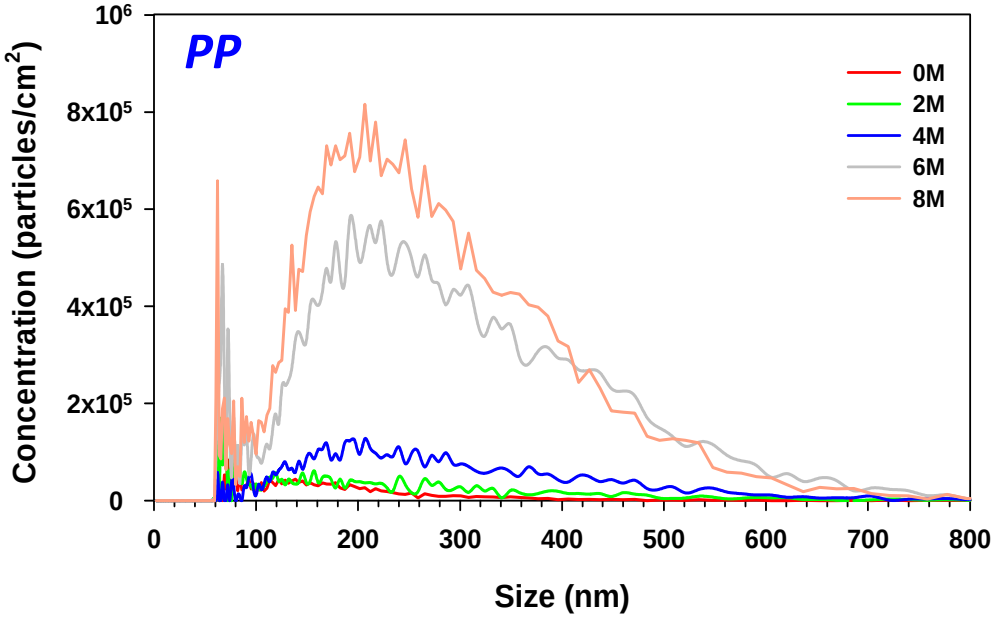
Produced nanoplastics and particle size distribution (<0.8 μm)_chamber

Particle size distribution





Exposure duration	Average size (nm)	
	LDPE	PP
0M	118	144
2M	131	165
4M	128	237
6M	151	240
8M	209	230

Song et al. (in preparation)

Discussion

In real beach environment,

- **Mechanical force (wind, wave, manual, etc.) could steeply increase fragmentation rate especially after certain level of photooxidation**
- **Exposure of sub-surface area after removal of the produced particles covering the surface may enhance further fragmentation process**
- **Shading effects (fouling, upside down, other objects, etc.) and cooling by wind may retard photooxidation and fragmentation process**

Conclusion

- Rapid fragmentation occurred at the EPS surface exposed to sunlight. Months' sunlight exposure is enough to produce nano- and micro-sized particles from EPS
- Large amount of nano-sized EPS particles (< 0.8 μm) was produced by sunlight exposure, but their mass contribution was negligible to the micro-sized particles (> 0.8 μm)
- Foamed plastic structure is very vulnerable for fragmentation by both the UV exposure and (or) mechanical abrasion

Further study

- Combined effects of UV exposure and mechanical force (e.g. vortexing w/ water, tumbling w/o water, pressing etc.)
- Weathering of other common polymers (PE, PP and PET) to estimate NMP production rate
- Weathering of other foamed plastics (foamed PU, PP, and PE)
- Effects of various environmental conditions on weathering rate of plastics
- Development of a prediction model for production of secondary microplastics from residual macroplastic debris in the environments by photochemical oxidation

Acknowledgement

Ministry of Oceans
and Fisheries

Thank you for
your attention!

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