Predicting plastic fragmentation in the environment

Using a mechanistic, open-source model

Sam Harrison
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13 June 2023

UK Centre for Ecology & Hydrology

BASF We create chemistry

Duke

UNIVERSITY OF AMSTERDAM

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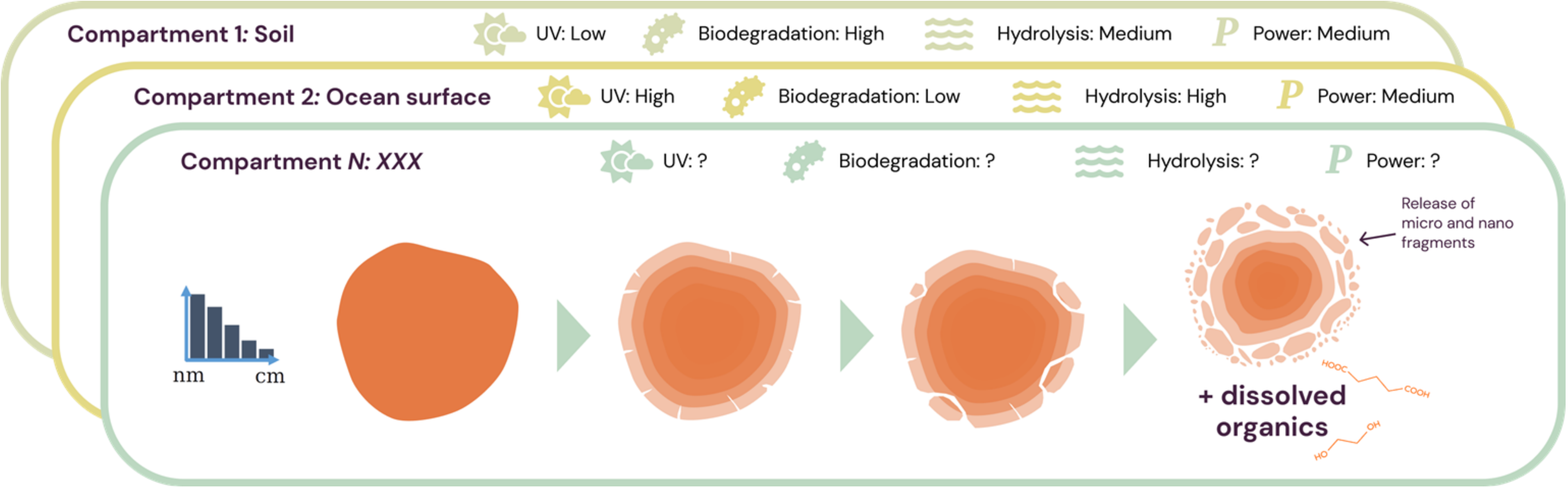
TL;DR

ECO59

A pragmatic, open-source, mechanistic model of **Micro and NanoPlastic FRAGMentation in the ENvironmenT**:

- Predicts the time evolution of particle size distributions and concentrations.
- Based on the principle that fragmentation rates depend on **polymer type**, **degradation state** and **environmental compartment**.



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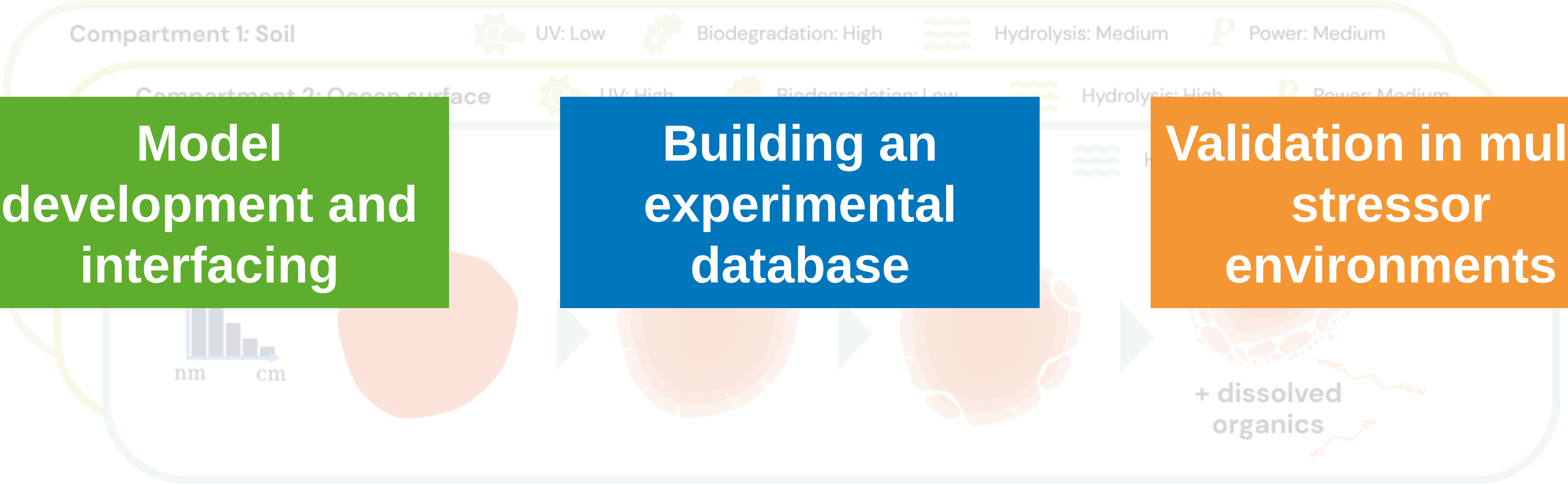


Model development and interfacing

Building an experimental database

Validation in multi-stressor environments

Model conceptualisation

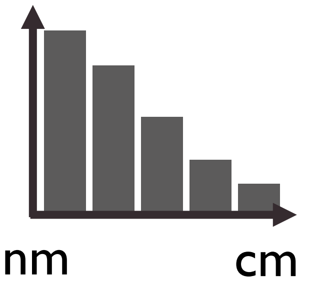
$$\frac{dc_k}{dt} = \Sigma_i k_{\text{frag},i} f_{i,k} n_i - k_{\text{frag},k} n_k$$ breakup (fragmentation)

$$- k_{\text{dis},k} n_k$$ “dissolution”

$$+ \frac{1}{2} \Sigma_{i+j \to k} \alpha_{i,j} \beta_{i,j} n_i n_j - \alpha_{B,k} \beta^M_{B,k} B n_k$$ aggregation

$$- k_{\text{sed},k} n_k$$ sedimentation

$$+ S_k$$ source



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Model conceptualisation

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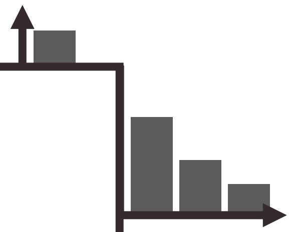
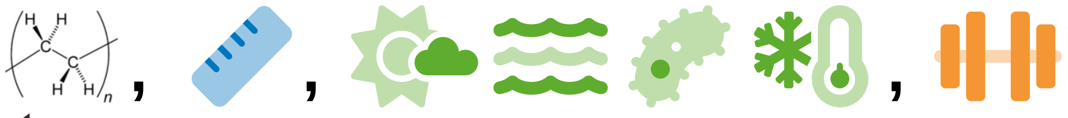
breakup (fragmentation)



$k_{\mathrm{frag}} = f($  $)$

and $f_{i,k}$

Polymer type, **Particle size**, **Degradation state**, **Mechanical abrasion power**

Building an experimental database

Populating the model with numerical degradation and fragmentation rates

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Experimental dataset and characterization

Stress		
Mechanical disruption (MD)	pristine	
Hydrolysis* (by immersion) +MD	22°C	10 days seawater 1 year seawater
	22 °C (BASF only)	10 days pH 4 10 days pH 9 10 days DI water
	22°C	100 days pH 4 100 days pH 9 100 days DI water
	0°C	100 days seawater
	22°C	100 days seawater
	65°C	100 days seawater
Photolysis +MD	BST 65°C (ISO4892 w/75%RH)	1000 h 1500 h 2000 h
	BST 90°C (Kalahari protocol)	1000 h 1500 h 2000 h
	BST 65°C (ISO4892 w/50%RH)	1000 h 1500 h 2000 h
Enzymatic Degradation	Enzymatic Incubation at 37°C or 55°C	1 day 10 day 100 day

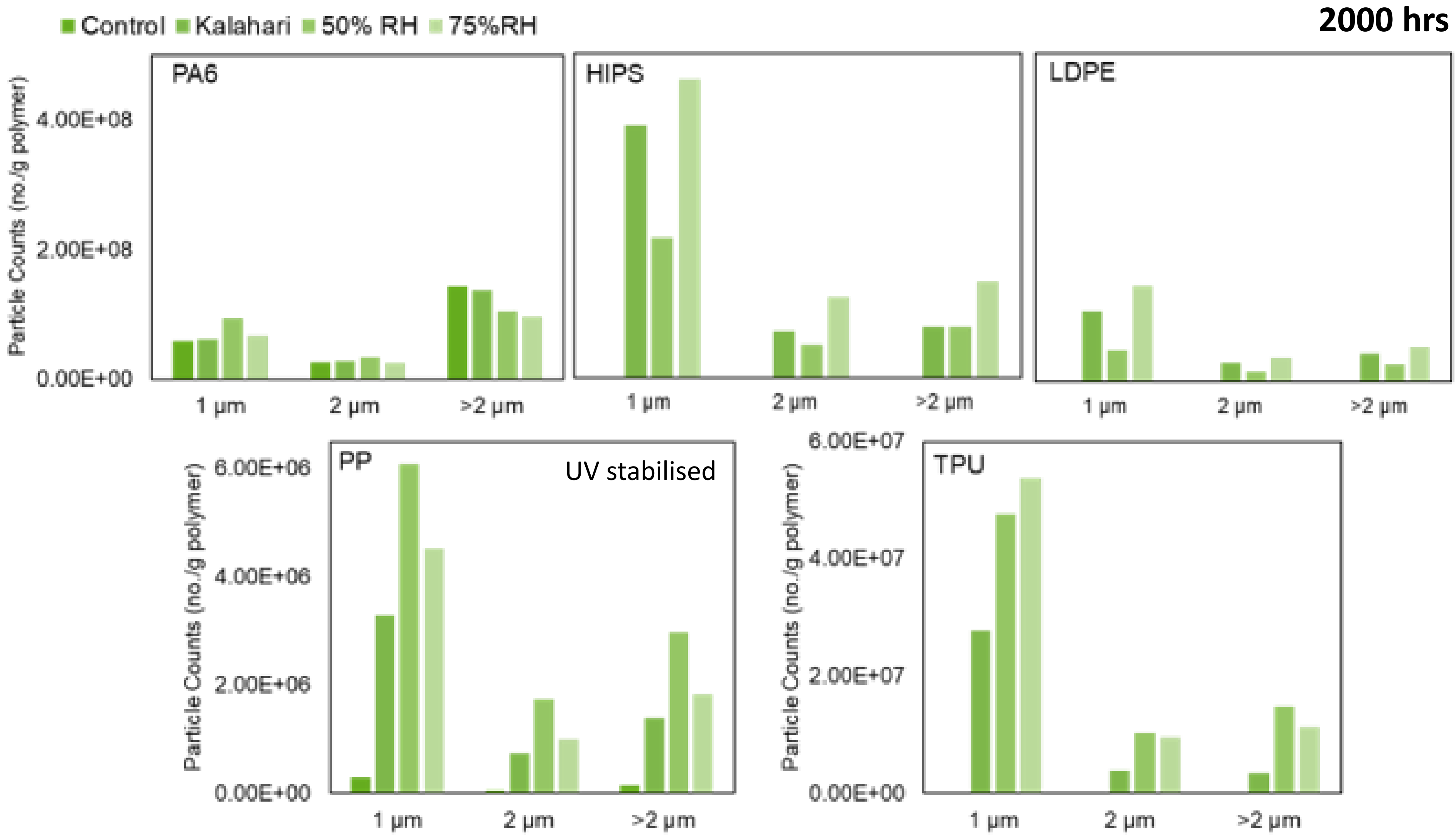
We vary: temperature, exposure duration, RH, salinity, pH

Polymers: TPU_ether_arom, PET, PLA, PP, LDPE, PA-6, HIPS

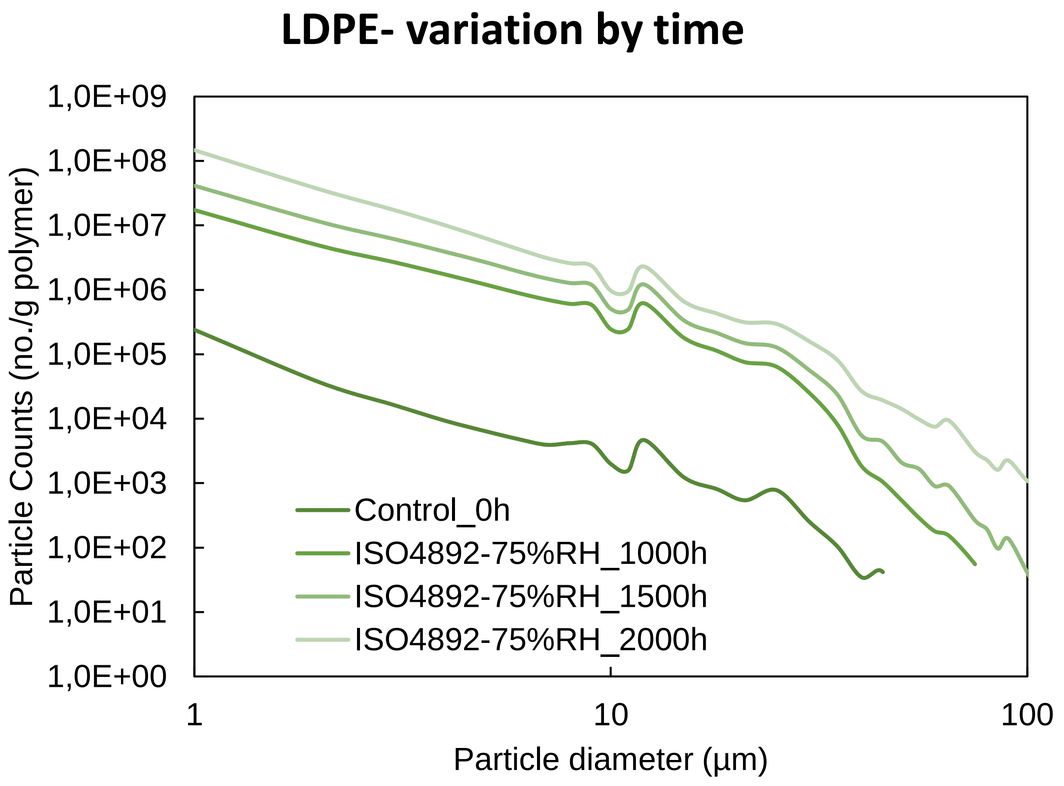
Various methods to obtain holistic understanding of fragmentation and degradation:

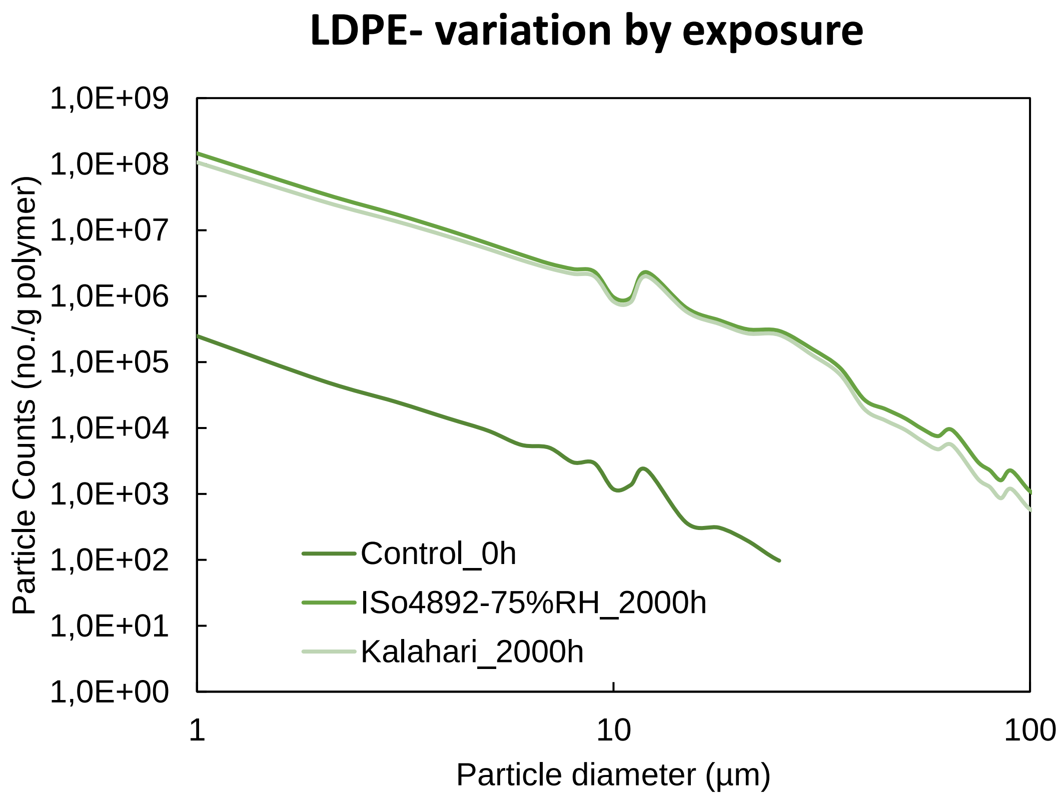
- Size distribution 0.01 to 1000 µm
  - AUC
  - Particle Counter (Abakus)
  - Mastersizer
- Mechanical & cracking
  - SEM
  - Abrasion
- Chemical aging, M_w, crystallinity
  - FTIR
  - GPC
  - DSC

Results highlights: Photolysis

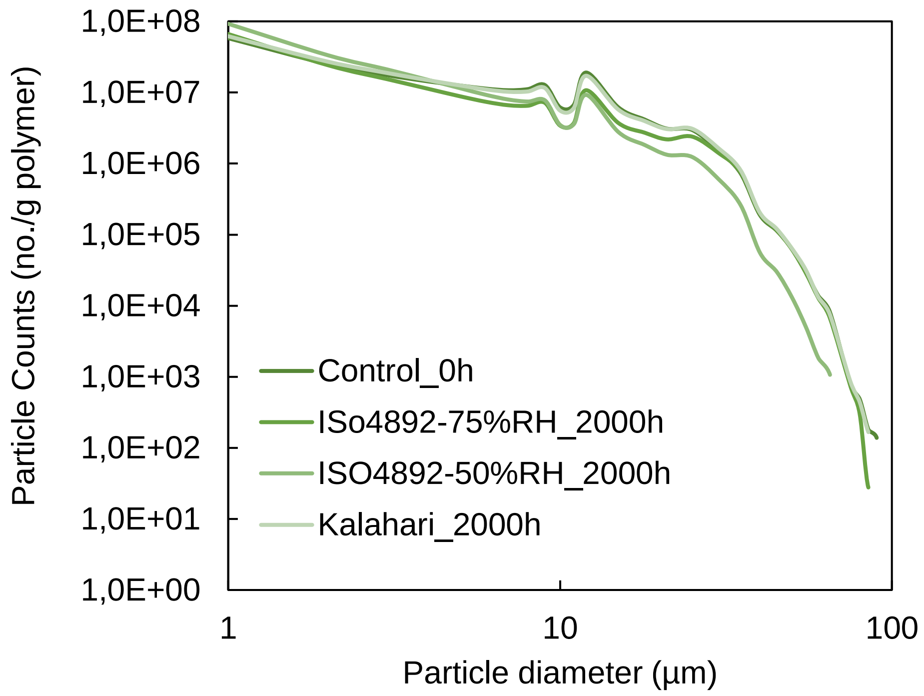


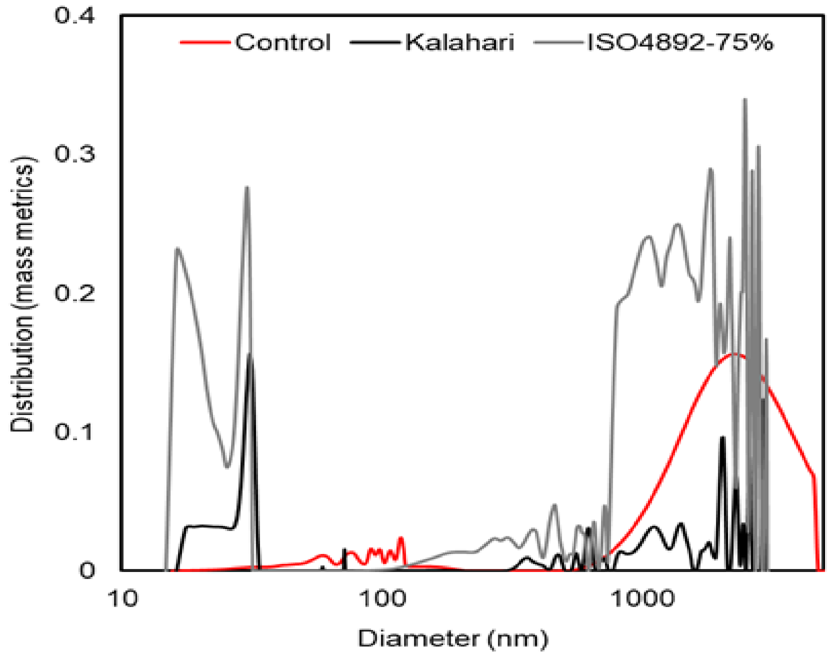
Results highlights: LDPE photolysis





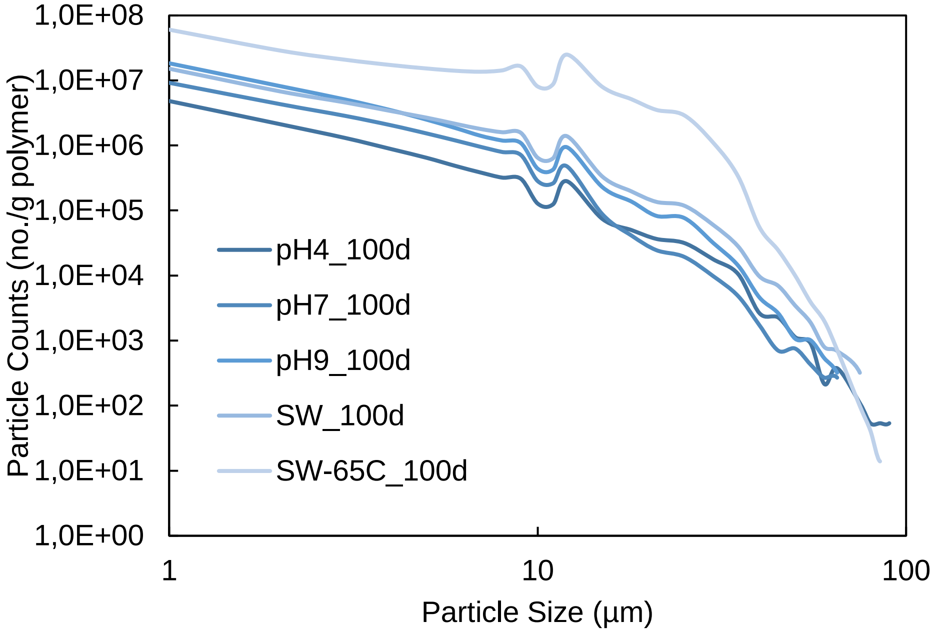
Results highlights: PA-6 Photolysis

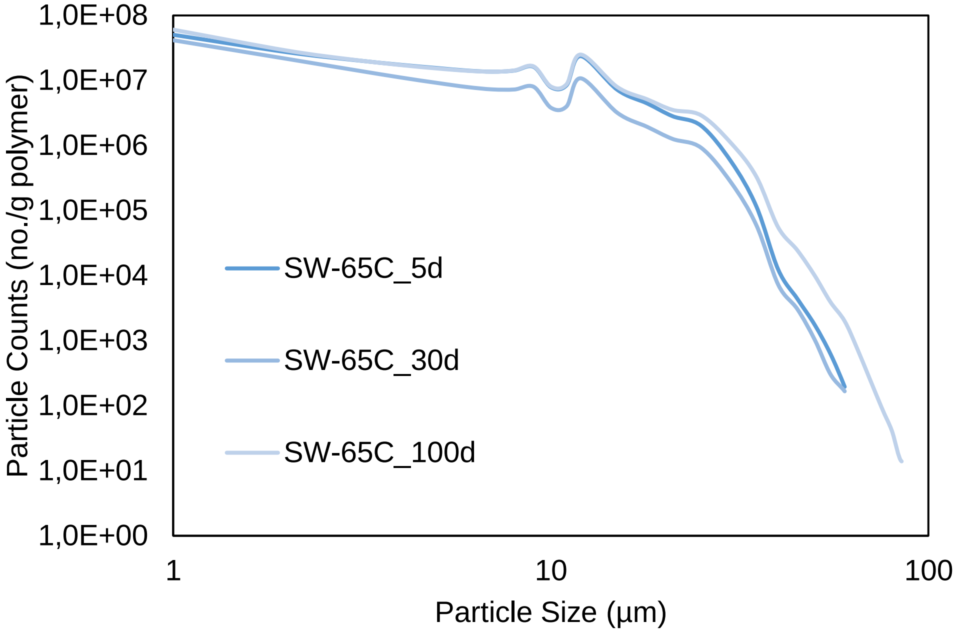




Sample description	Carbonyl Index (-)	DOC (mg/kg)	Number average Mn (g/mol)	Weight average Mw (g/mol)	Dispersity Mw/Mn (-)
PA6_0h	0.034	330	16 400	57 900	3.5
PA6_ISO4892_90C_2000h	0.411	3700	2 770	12 000	4.3
PA6_ISO4892_50%RH_2000h	0.400	-	2 350	8 990	3.8
PA6_ISO4892_75%RH_2000h	0.532	6100	2 130	8 130	3.8

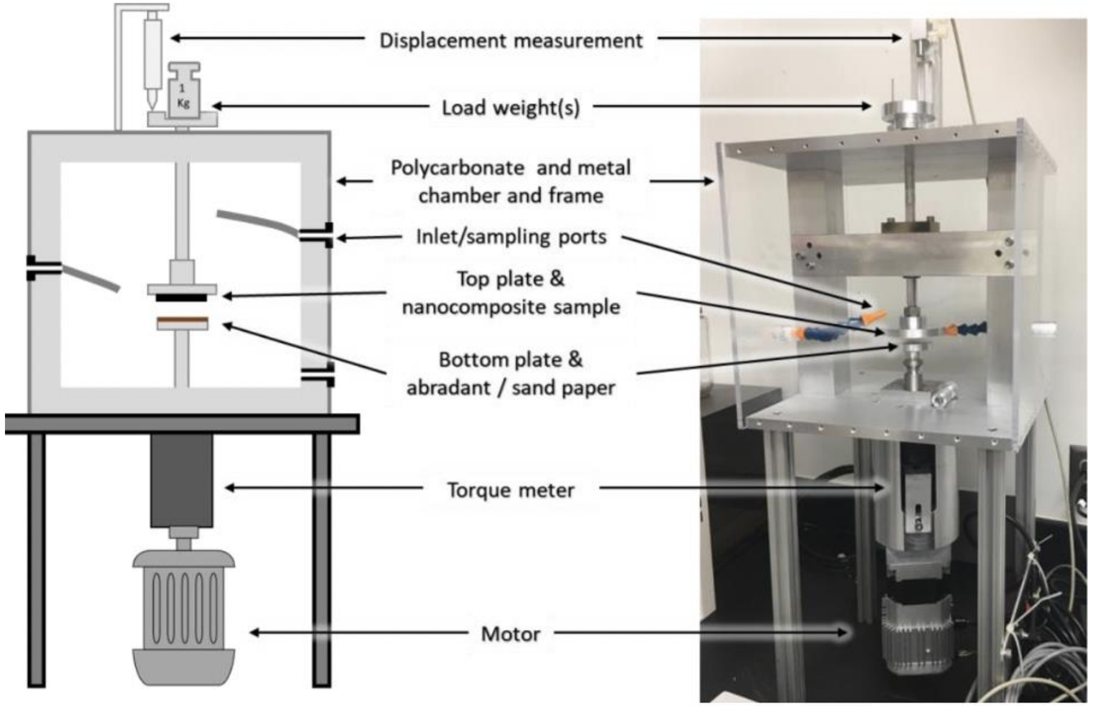
Results highlights: PA-6 hydrolysis

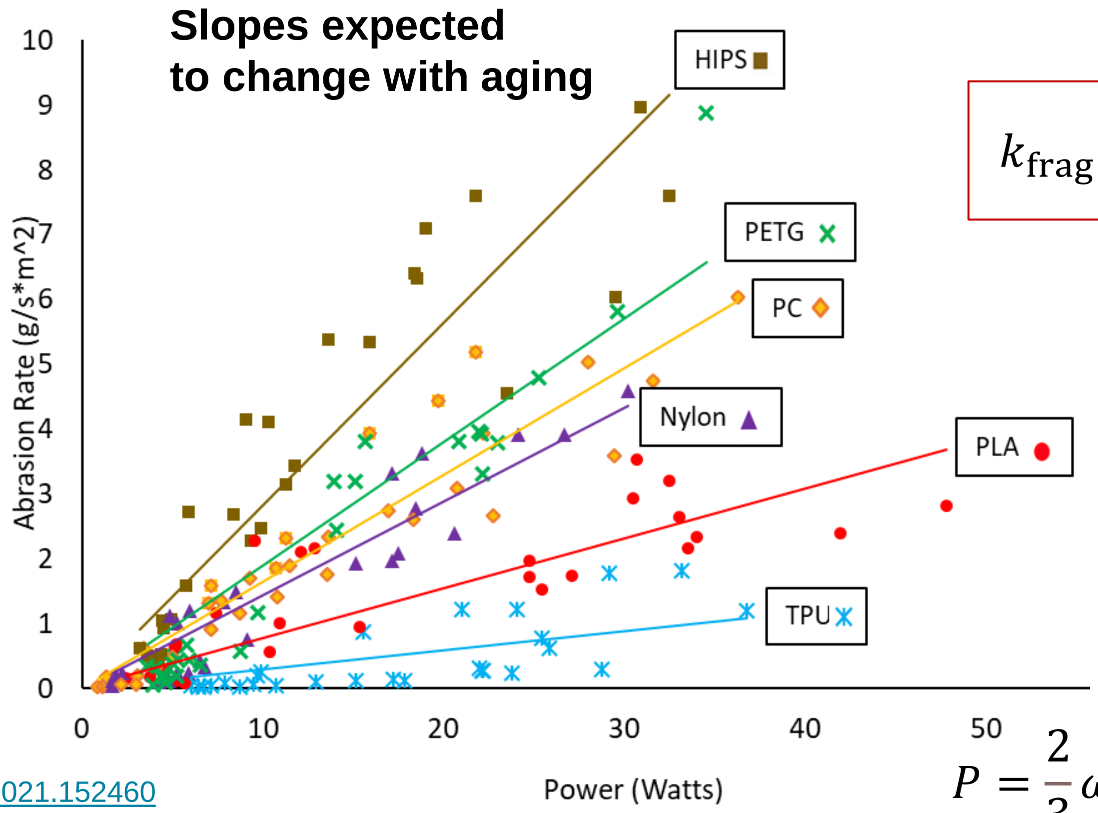




Mechanical abrasion to determine fragmentation rates

- Relates input power to mechanical abrasion rate, M, and thereby fragmentation rate.
- Will be applied to coupons of varying degradation states. Power scalable to environmental compartment.





$$k_{\text{frag}} = \frac{M}{\rho_c} \frac{6}{d_k}$$

$$P = \frac{2}{3} \omega r N \mu_f$$

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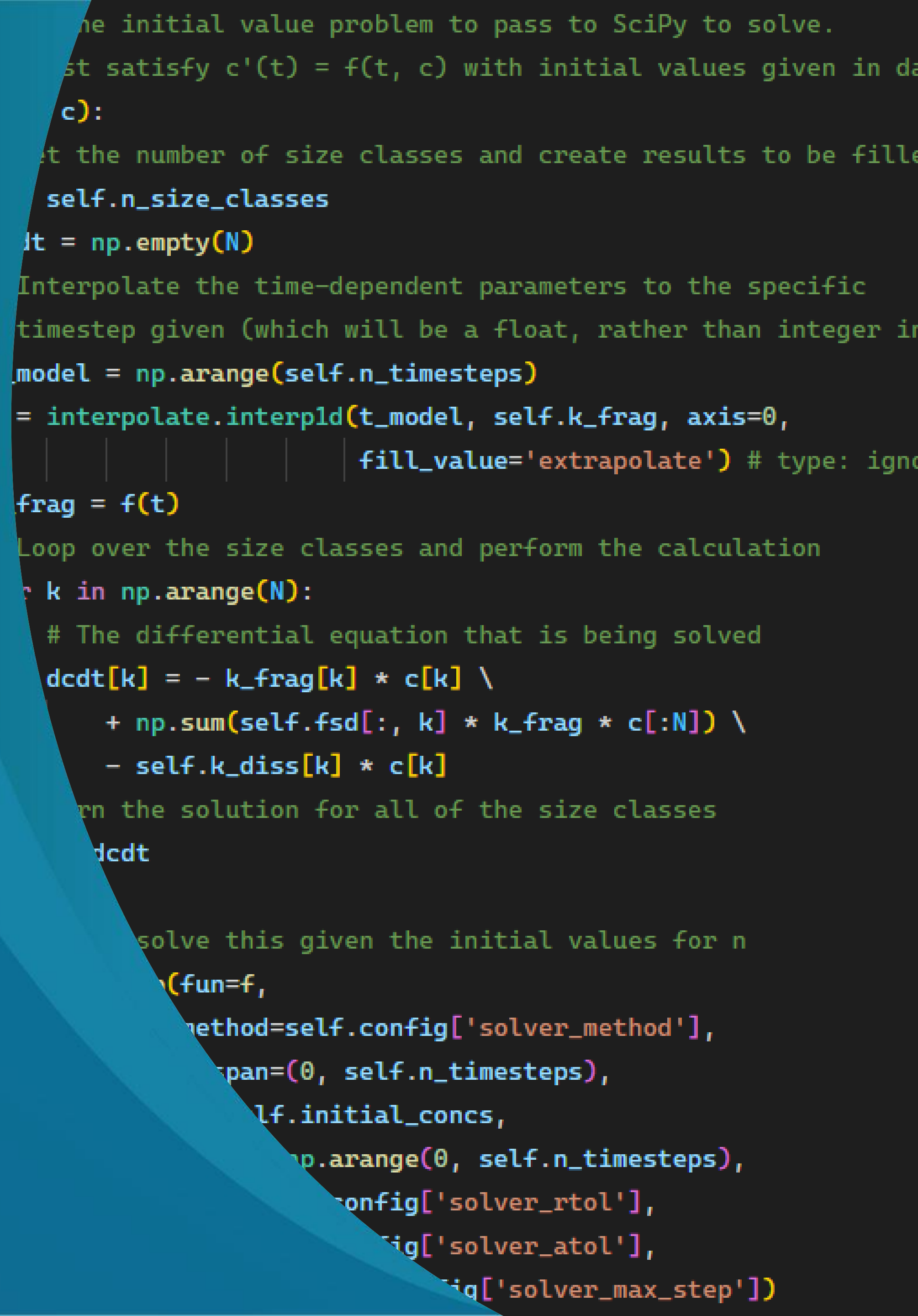
Joana Sipe et al., 2022
https://doi.org/10.1016/j.scitotenv.2021.152460

Model development

Developing, applying and rationalising a mechanistic model of microplastic fragmentation



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Model – Python package and documentation

Documentation:
https://microplastics-cluster.github.io/fragment-mnp

Python package:

```
$ pip install git+https://github.com/microplastics-cluster/fragment-mnp.git
```

Demo:
https://fragmentmnp.samharrison.science

FRAGMENT-MNP

Search this book...

FRAGMENT-MNP

USERS

- Example usage
- Model configuration
- Input data
- Plotting
- Advanced usage

DEVELOPERS

- Developers quickstart
- Developing with Conda
- API Reference

Example usage

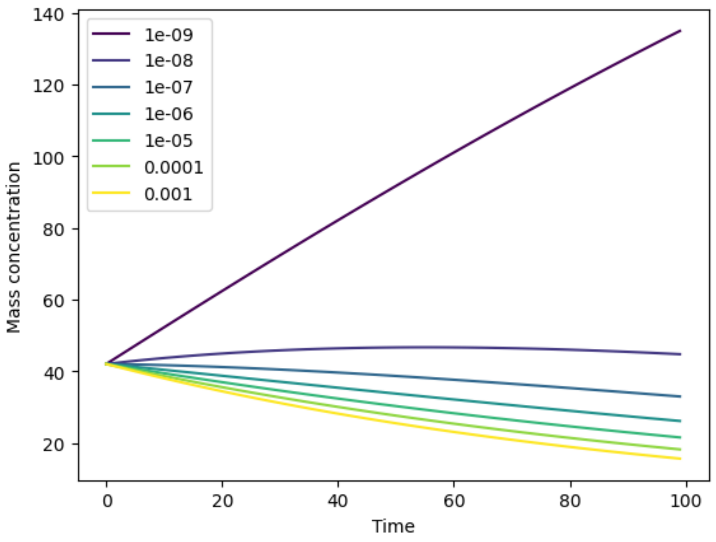
Running the FRAGMENT-MNP model is a two-step process. First, the model must be initialised by passing it config and input data. Example config and data is given in the `fragmentmnp.examples` module, which is used here. Then the `FragmentMNP.run()` method runs the model and returns a `FMNPOutput` object with the output data.

```python
from fragmentmnp import FragmentMNP
from fragmentmnp.examples import minimal_config, minimal_data
import matplotlib.pyplot as plt
import numpy as np

# Create the model and pass it config and data. minimal_config and
# minimal_data are an examples of a dicts with only required values.
# full_{config|data} are examples of a dicts with all values given
fmnp = FragmentMNP(minimal_config, minimal_data)
# Run the model
output = fmnp.run()
```

The returned `FMNPOutput` object contains a timeseries `t`, particle mass and number concentrations for each size class, `c` and `n`, particle number concentration lost from each size class due to dissolution `n_diss`, and corresponding concentration of dissolved organics from each size class `c_diss`. See the API reference for full details. A convenient plotting function can be used to quickly plot model output (see Plotting):

```python
# Plot the time evolution of mass concentrations
_ = output.plot()
```



Model parameters

Internal parameters the control the model

Model can be calibrated against experimental data to give values to these parameters.

End goal is external parameters requirements that are pragmatic – e.g. polymer type, density, environmental compartment

Config

```
{'dt': 1,
 'n_size_classes': 7,
 'n_timesteps': 100,
 'particle_size_range': [-9, -3],
 'solver_atol': 1e-06,
 'solver_max_step': inf,
 'solver_method': 'RK45',
 'solver_rtol': 0.001,
 'k_diss_scaling_method': 'constant'}
```

Data

```
{'k_diss': 0.0,
 'k_diss_gamma': 1.0,
 'density': 1380,
 'fsd_beta': 0.0,
 'initial_concs': 42,
 'k_frag': 0.01,
 'k_frag_tau': 0.0,
 'theta_1': 0.0}
```

Model parameters

Controls the size bins, size range and time span modelled

Config for the numerical solver

Controls rate and size dependence of dissolution

Controls how fragmenting mass is split between daughter size classes

Controls fragmentation rate and its size and time dependence

Config

```
{'dt': 1,
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```
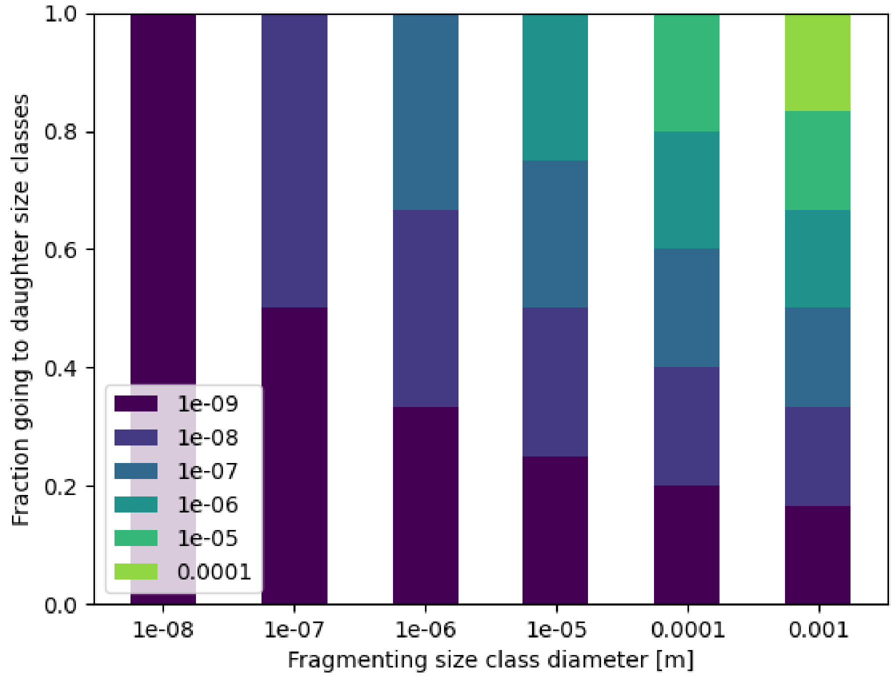
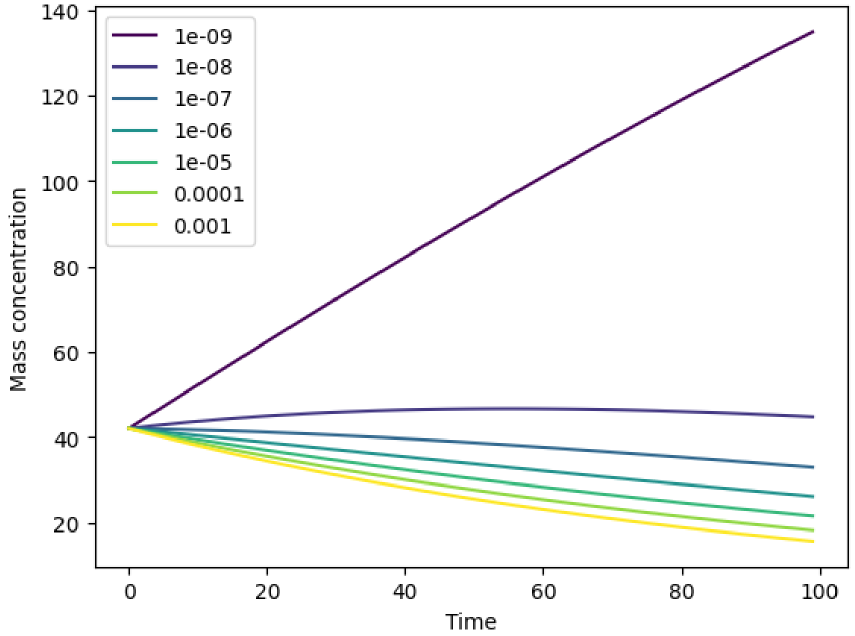

Model – fragment size distribution

Parameter β_{FSD} controls the split of fragmenting mass to daughter size fractions.

$\beta_{\mathrm{FSD}} = 0$

Even split to daughter size classes





$\beta_{\mathrm{FSD}} < 0$

Higher proportion goes to smaller size classes

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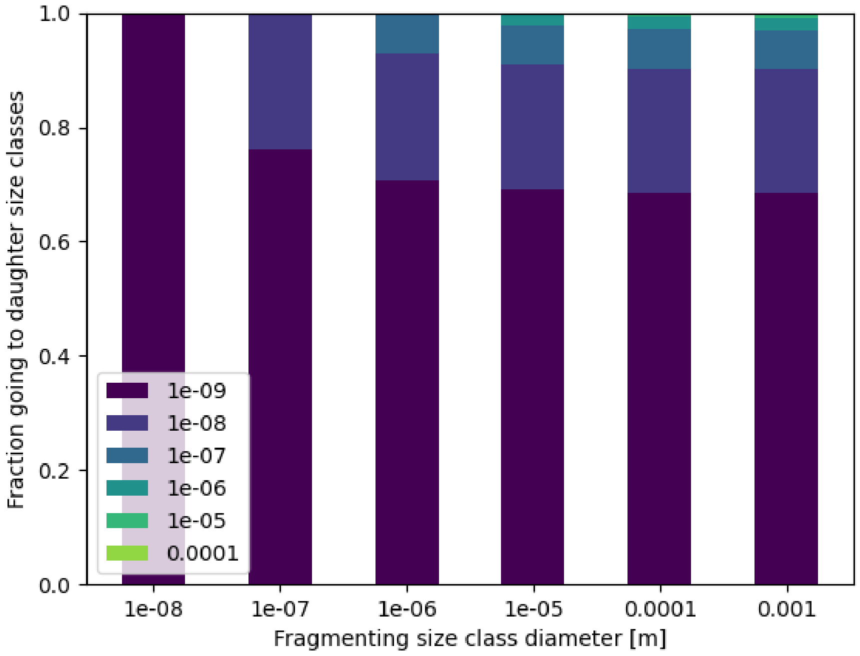

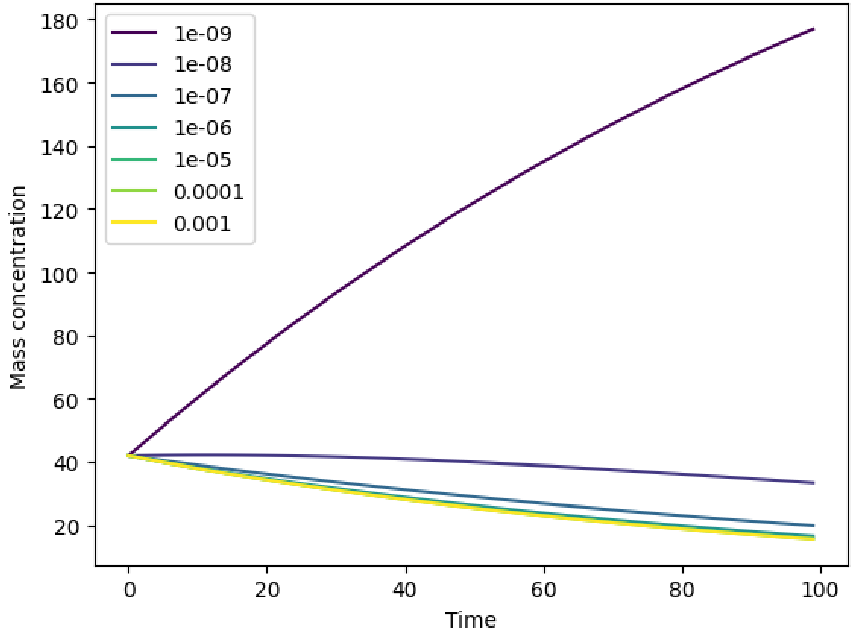

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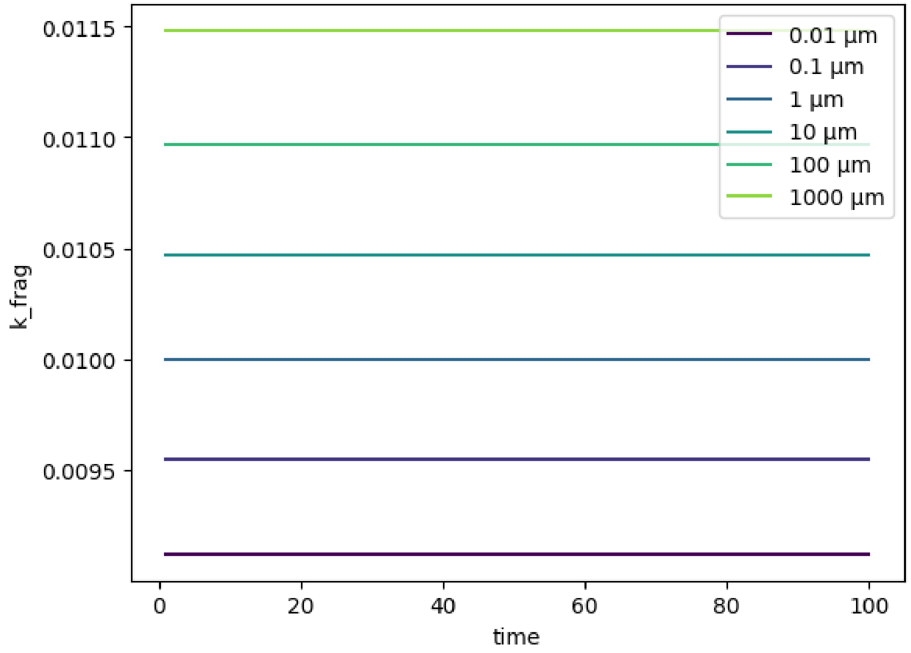
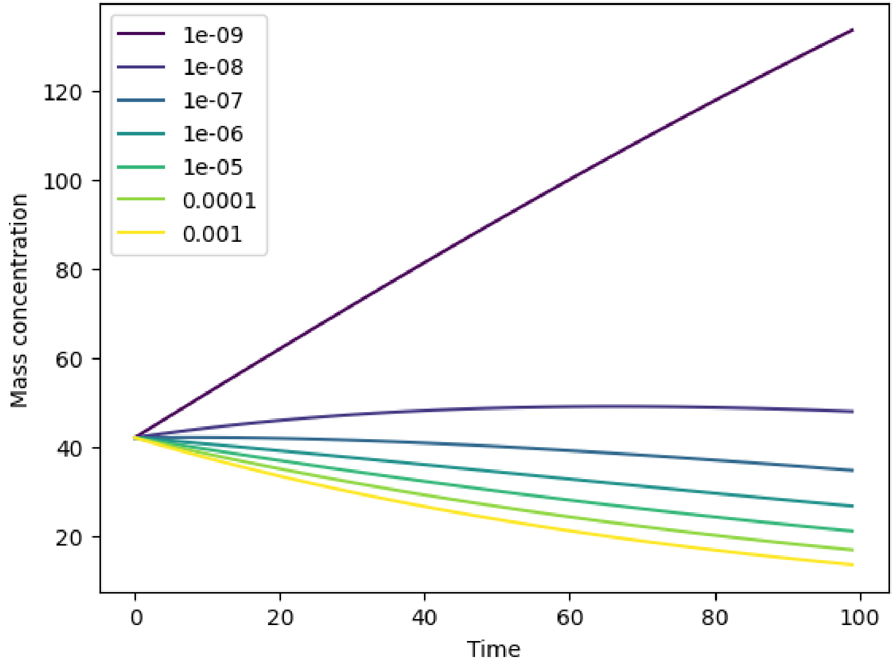
Model – time-dependent fragmentation rate

Parameter $\tau_{k_{\text{frag}}}$ controls the time-dependence of the fragmentation rate.

$\tau_{k_{\text{frag}}} = 0$

Constant fragmentation size





$\tau_{k_{\text{frag}}} < 0$

Decreasing fragmentation rate

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Model – time-dependent fragmentation rate

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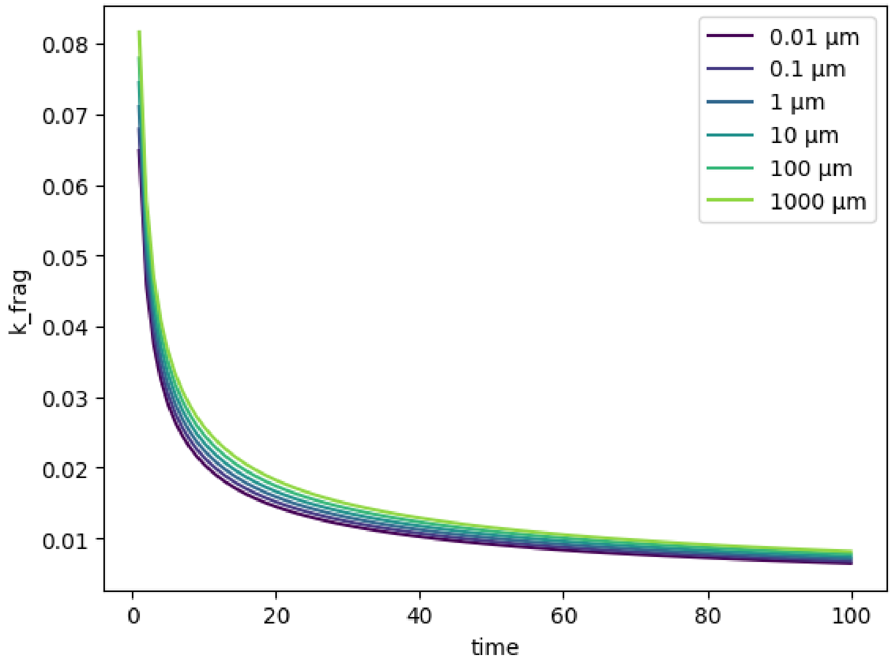
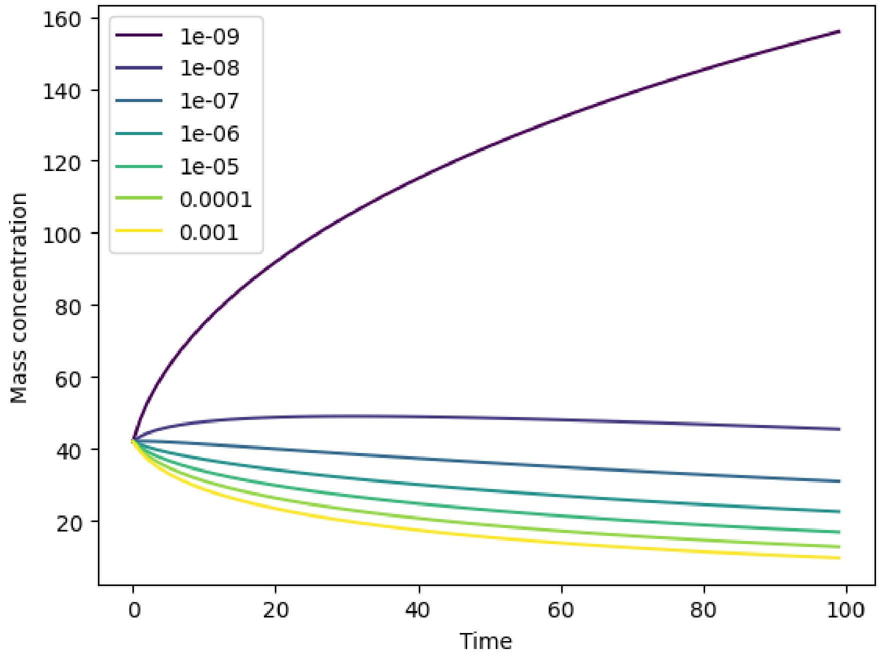
Constant fragmentation size

$\tau_{k_{\text{frag}}} < 0$

Decreasing fragmentation rate





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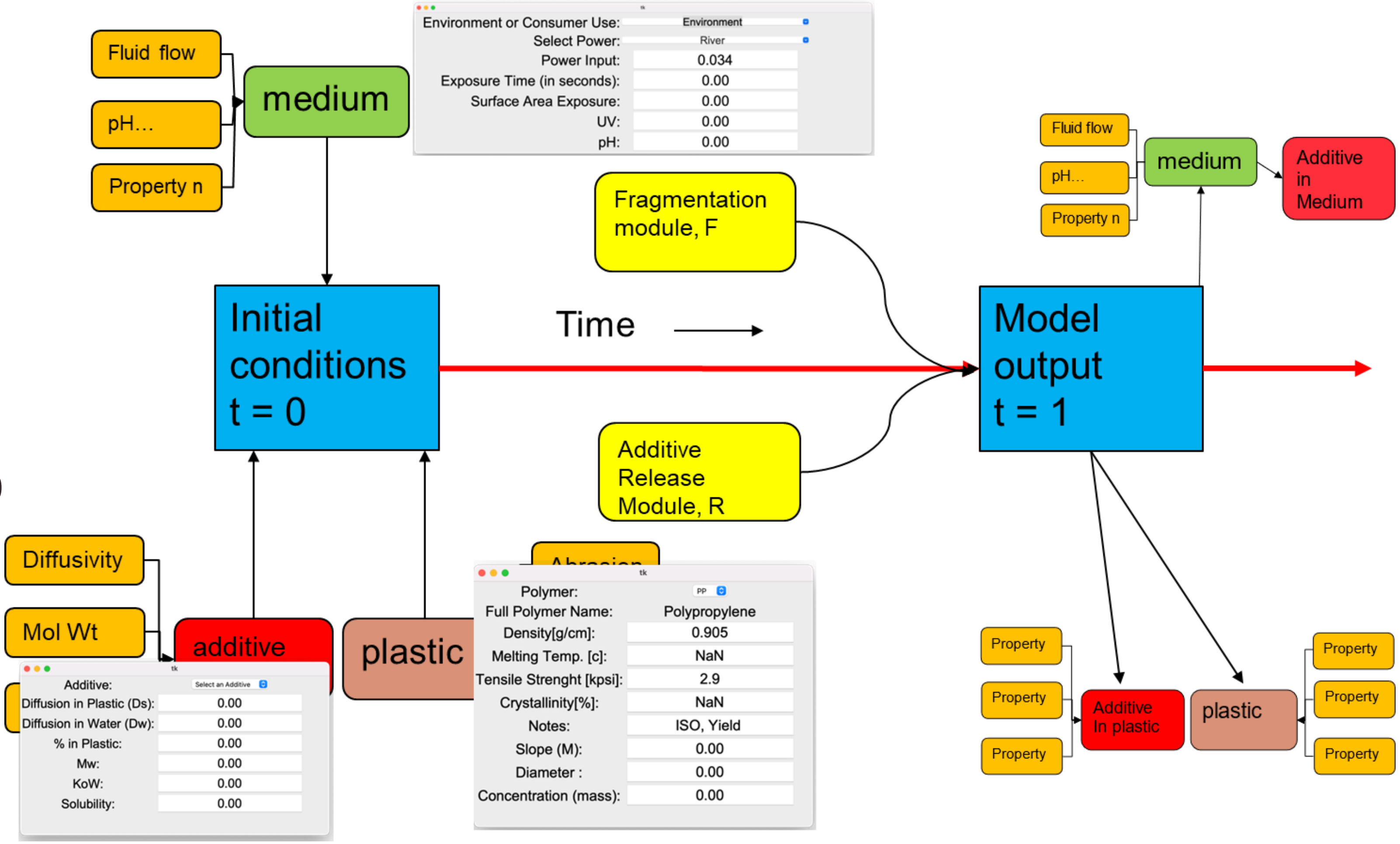
Data integration

Using experimental data to parametrise the model based on a set of pragmatic external parameters.

Stats model to fit relationship between external params (e.g. polymer phys-chem) and internal (e.g. fragmentation rate)



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Ground truthing

Validation of model predictions by measured fragment size distributions

- Data from literature and other projects on microplastics in the environment.
- Three-dimensional shaking with glass beads.
- Plant root experiments to see the influence of root action in prompting fragmentation

Polymer at soil surface (Control)

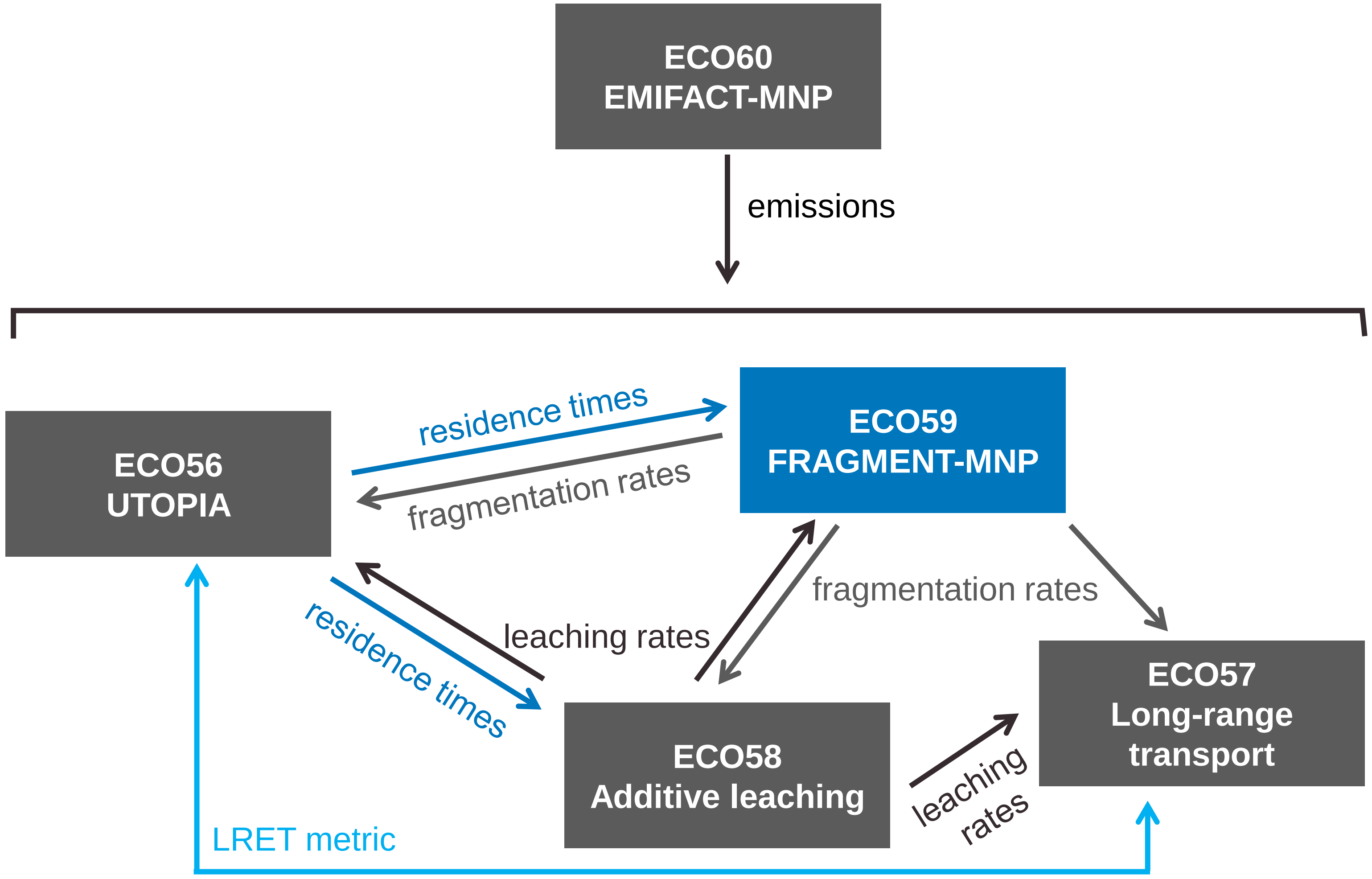
Polymer at the rhizosphere of *Vicia sativa* (a legume)

Polymer at the rhizosphere of *Triticum aestivum* (Wheat, a cereal)

✓ **Both pristine and UV-exposed polymers (PLA, PET, TPU, and LDPE) will be exposed to the two plants over an active growing period of 8 months.**

✓ **Characterisation of polymers fragmentation and degradation will be done every 2 months.**

Integration with other projects



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Summary

- Prototype model completed with iterative improvements through the rest of the project (May 2024).
- Building experimental database in progress – most experiments completed, data integration to be done.
- End result will be model with pragmatic input requirements that predicts time evolution of polymer size distributions in environmental compartments.
- The model will be able to provide realistic fragmentation rates and distributions to fate and exposure models, + even more if integrated with additive release model…

Thank You

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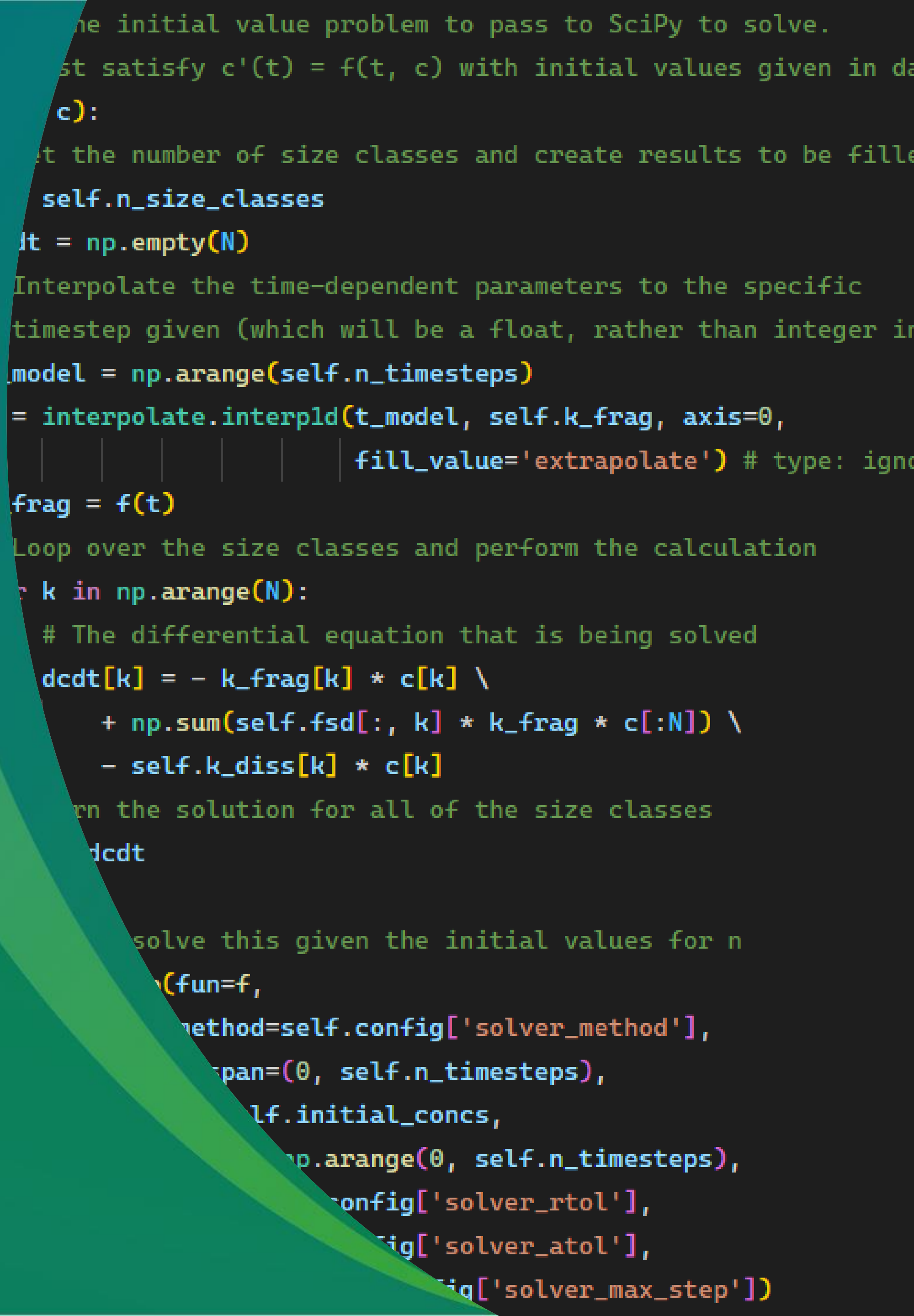

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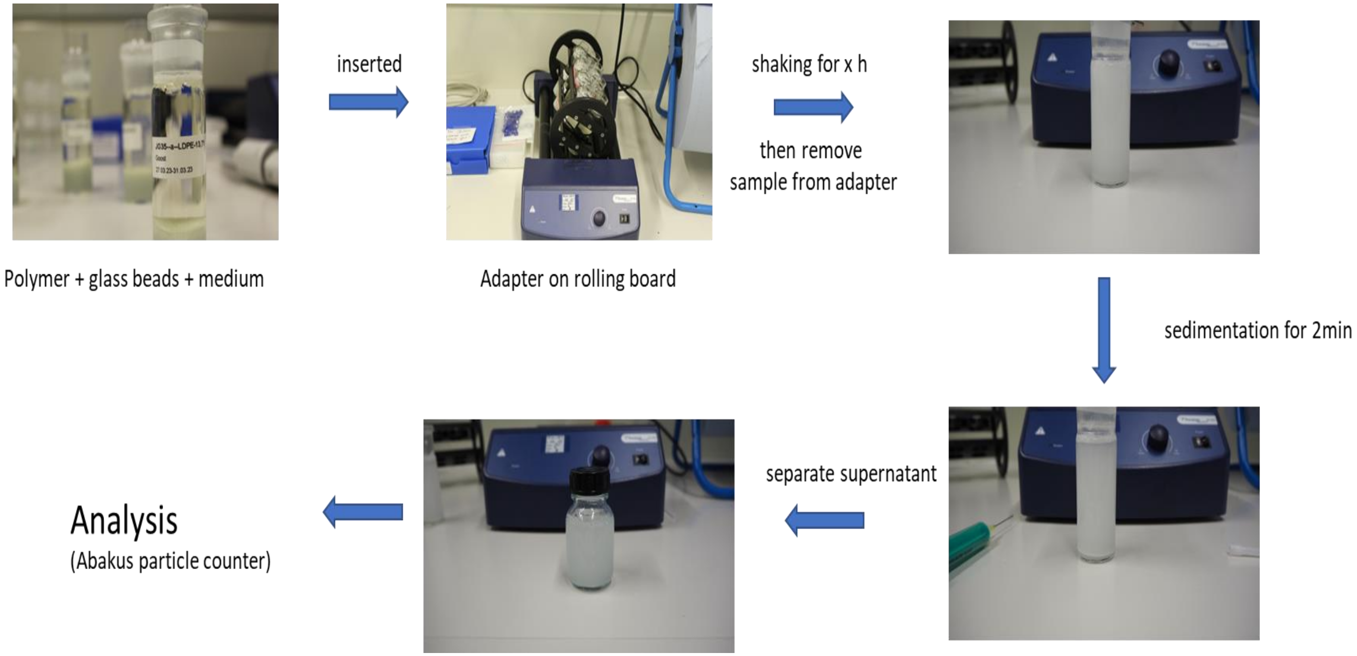
Glass bead shaking



Polymer	State	Medium	Glass beads [g]	power [Watts]	Time [h]
PA6	pristine	DI-water	0	0	3,5
PA6	pristine	DI-water	4,39	2	3,5
PA6	pristine	DI-water	13,71	15-20	3,5
PA6	pristine	DI-water	20,57	40-75	3,5
PA6	aged	DI-water	0	0	3,5
PA6	aged	DI-water	4,39	2	3,5
PA6	aged	DI-water	13,71	15-20	3,5
PA6	aged	DI-water	20,57	40-75	3,5
LDPE	pristine	DI-water	0	0	3,5
LDPE	pristine	DI-water	4,39	2	3,5
LDPE	pristine	DI-water	13,71	15-20	3,5
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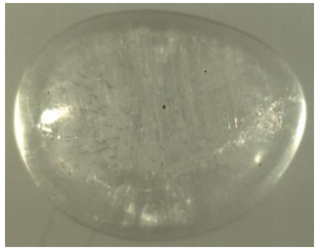
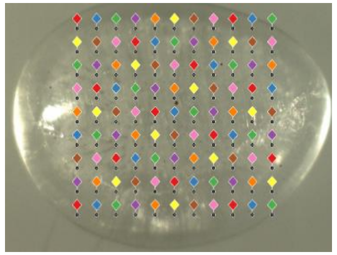
-	-	DI-water	4,39	-	3,5
-	-	DI-water	13,71	-	3,5
-	-	DI-water	20,57	-	3,5

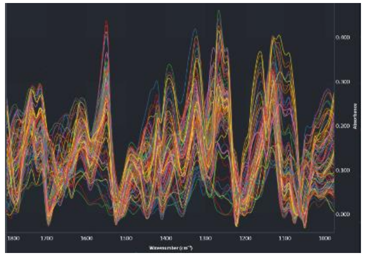
Assessment of polymers fragmentation rates at the rhizosphere

Surface characterisation by Infra-red spectroscopy

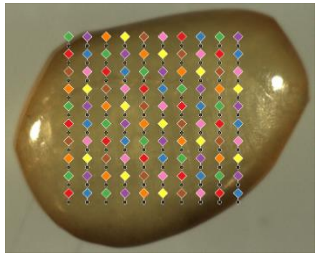
Pristine PLA

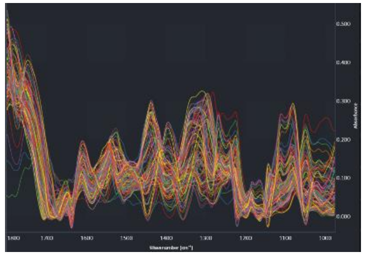




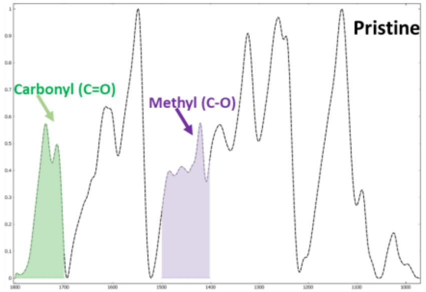


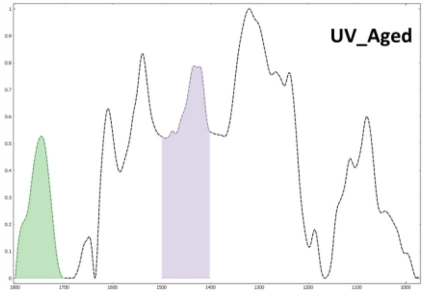
UV-exposed (ISO 4892-2: 1000 hrs) PLA

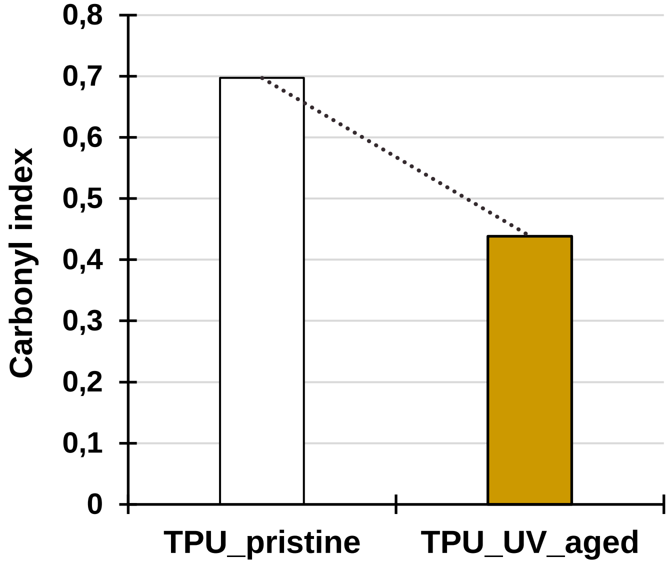




Degradation assessment by Carbonyl index calculation (the ratio of the carbonyl to the methyl region)

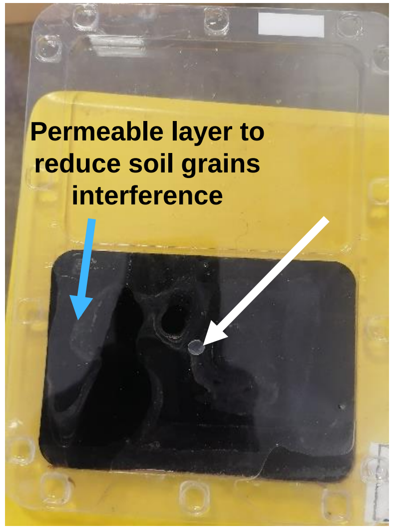






Calculation of carbonyl index suggests UV degradation reduces PLA CI by 37%

Polymer at soil surface (Control)

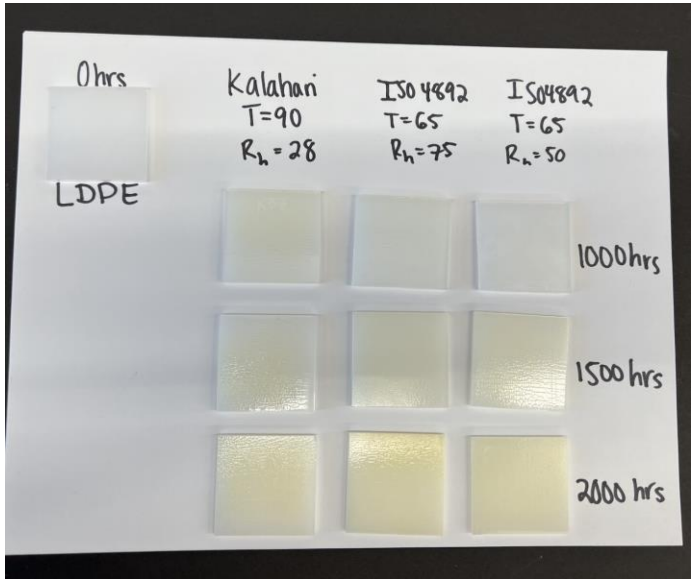


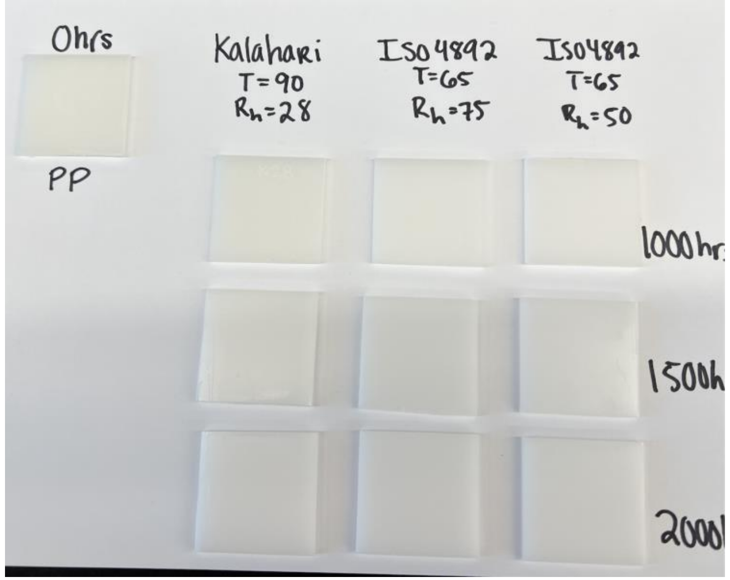
Polymer at the rhizosphere of *Vicia sativa* (a legume)

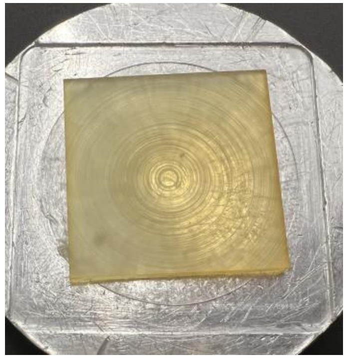
Polymer at the rhizosphere of *Triticum aestivum* (Wheat, a cereal)

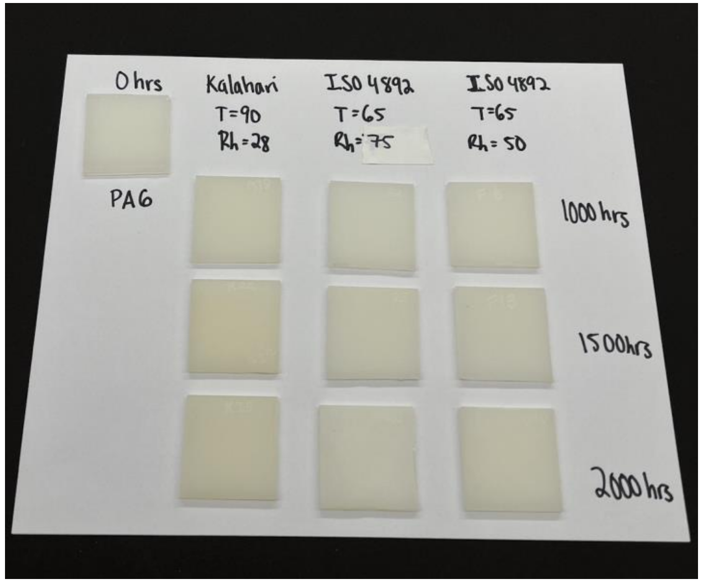
- ✓ Both pristine and UV-exposed polymers (PLA, PET, TPU, and LDPE) will be exposed to the two plants over an active growing period of 8 months.
- ✓ Characterisation of polymers fragmentation and degradation will be done every 2 months.

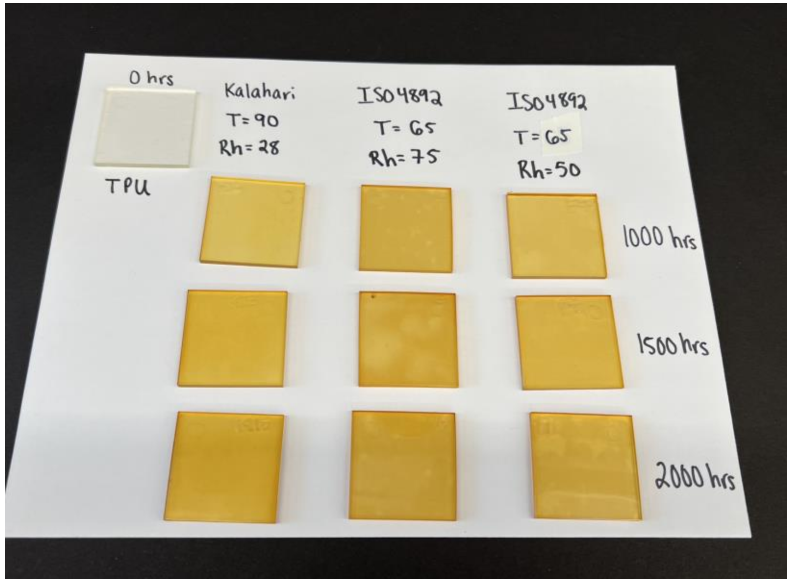
Images of Photolysis Plastic for reference

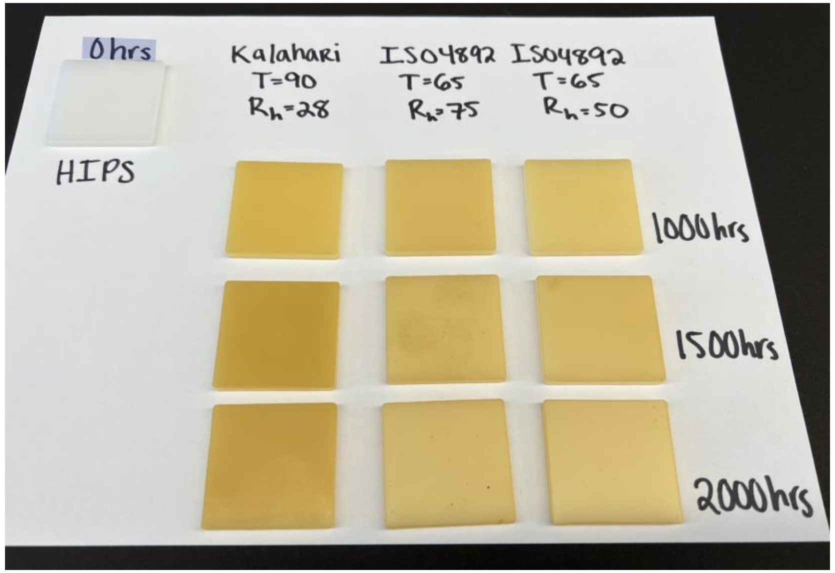




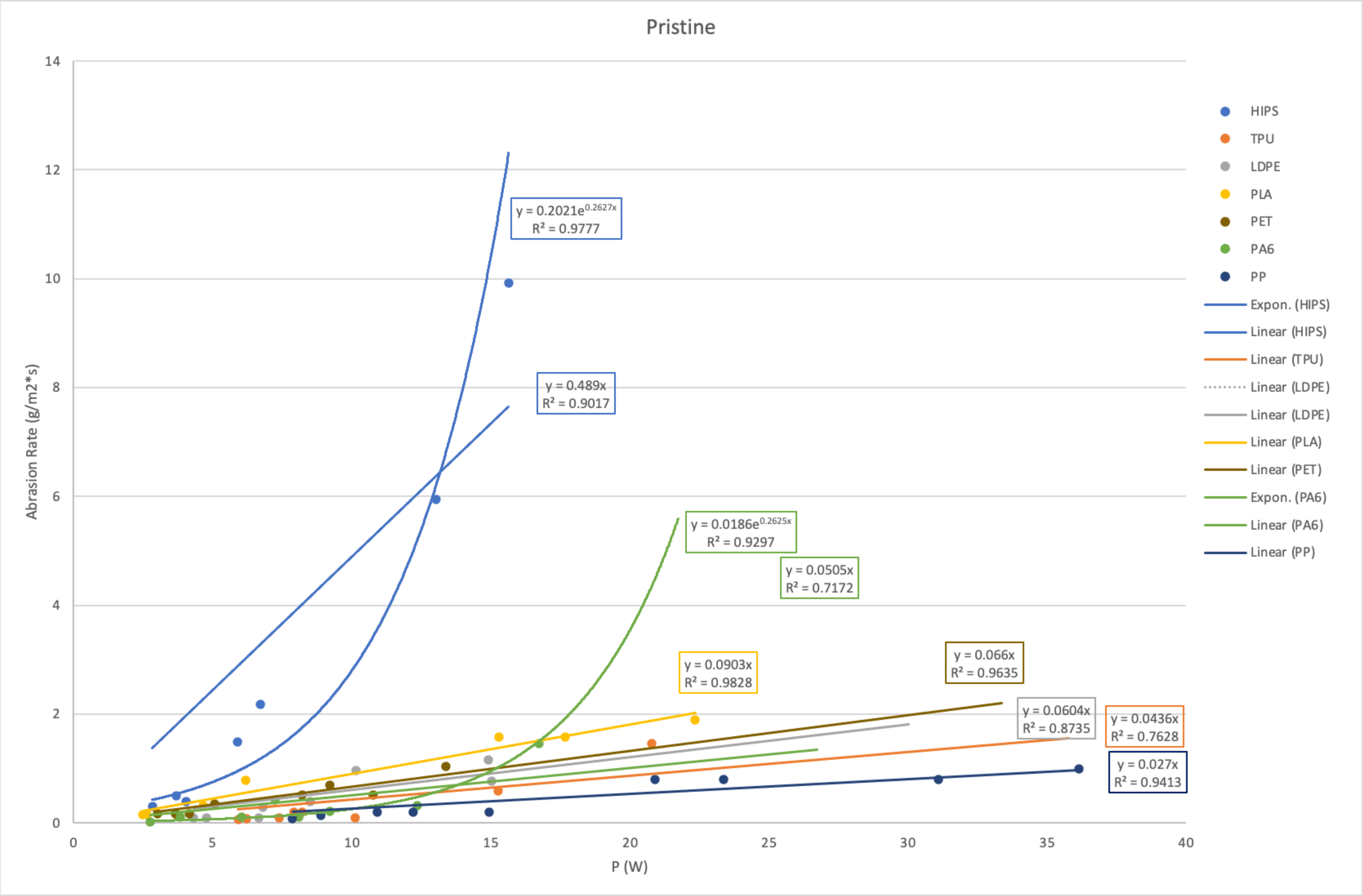




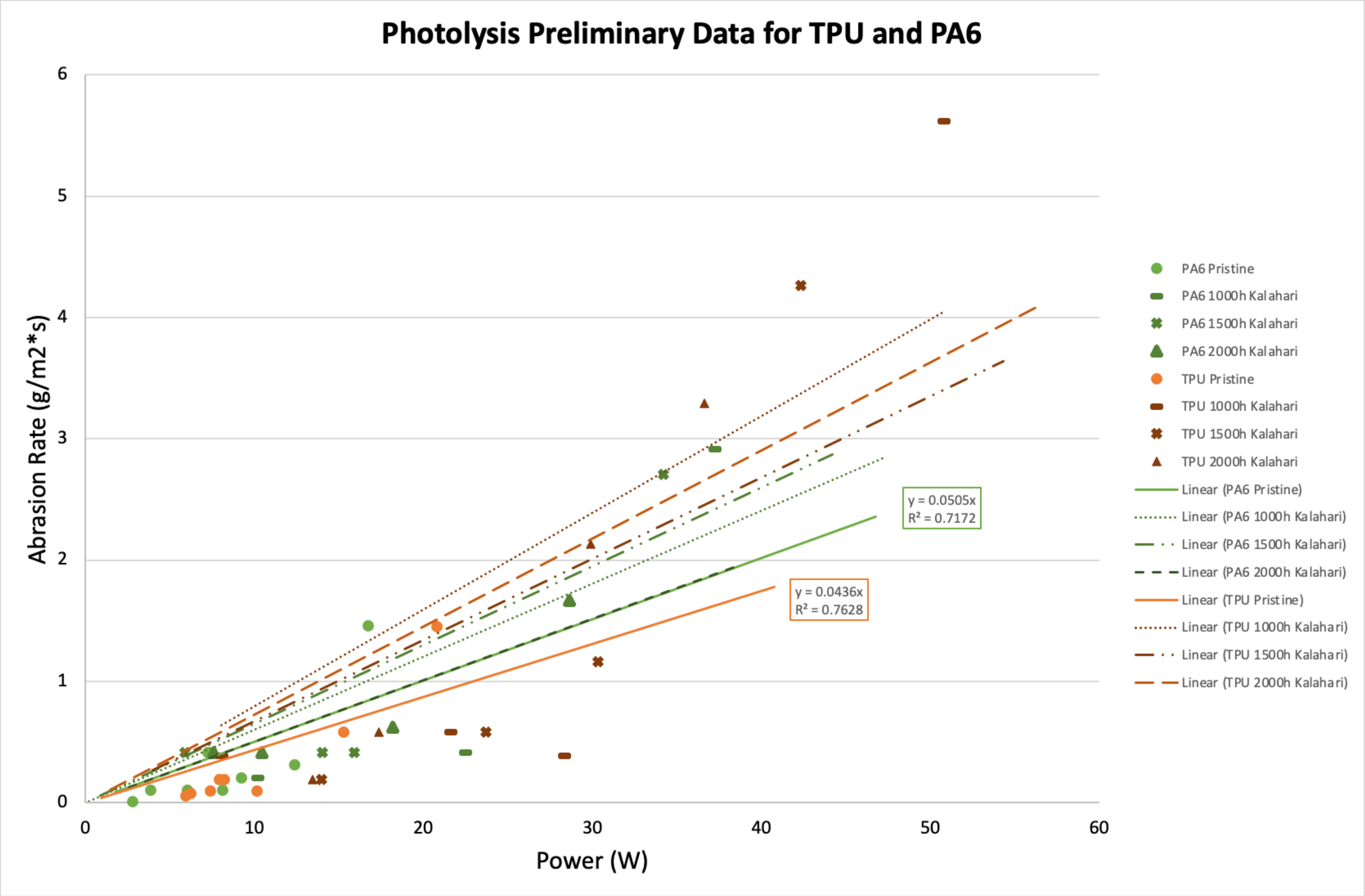




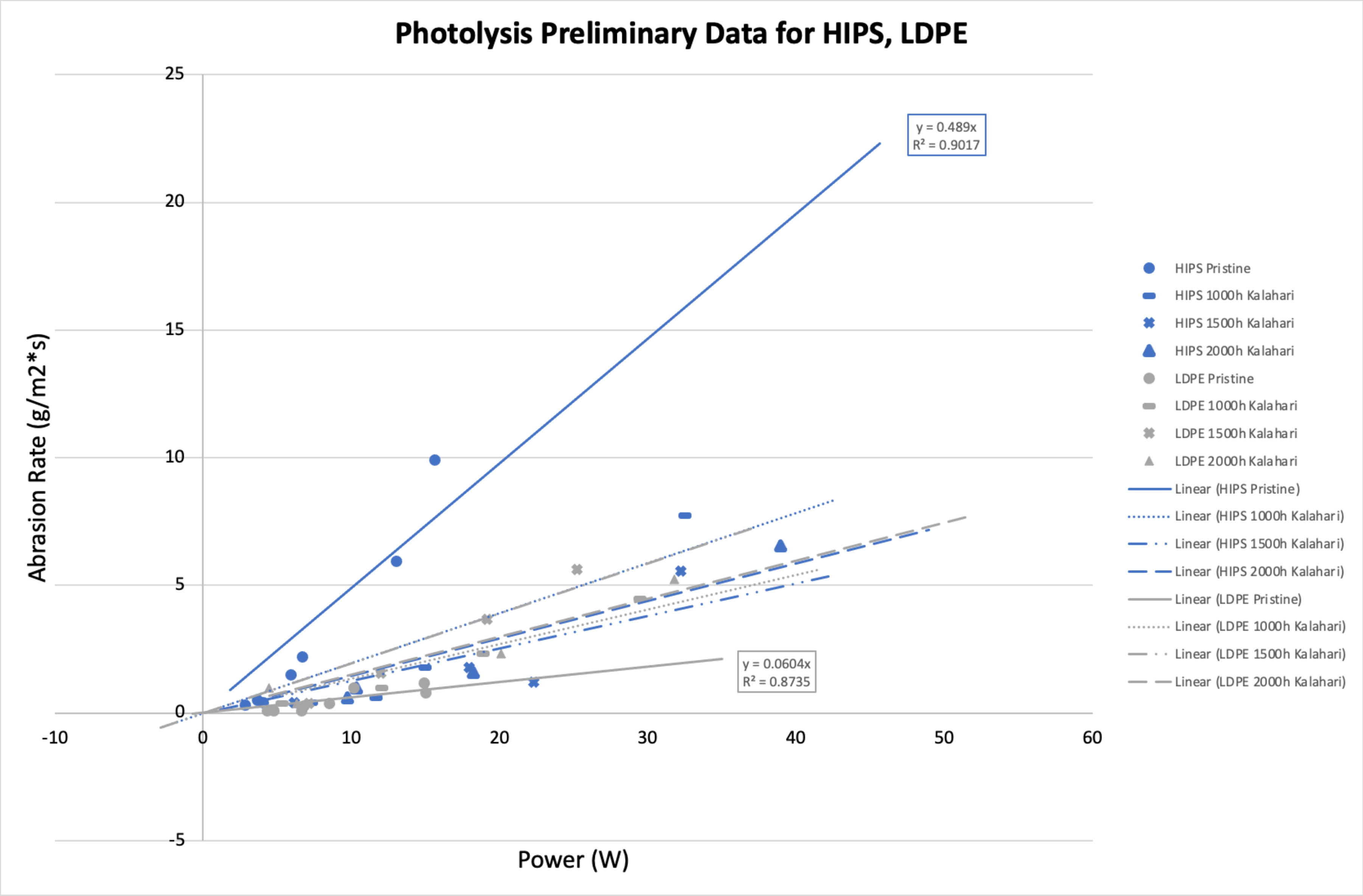
Pristine Plastic with replicate



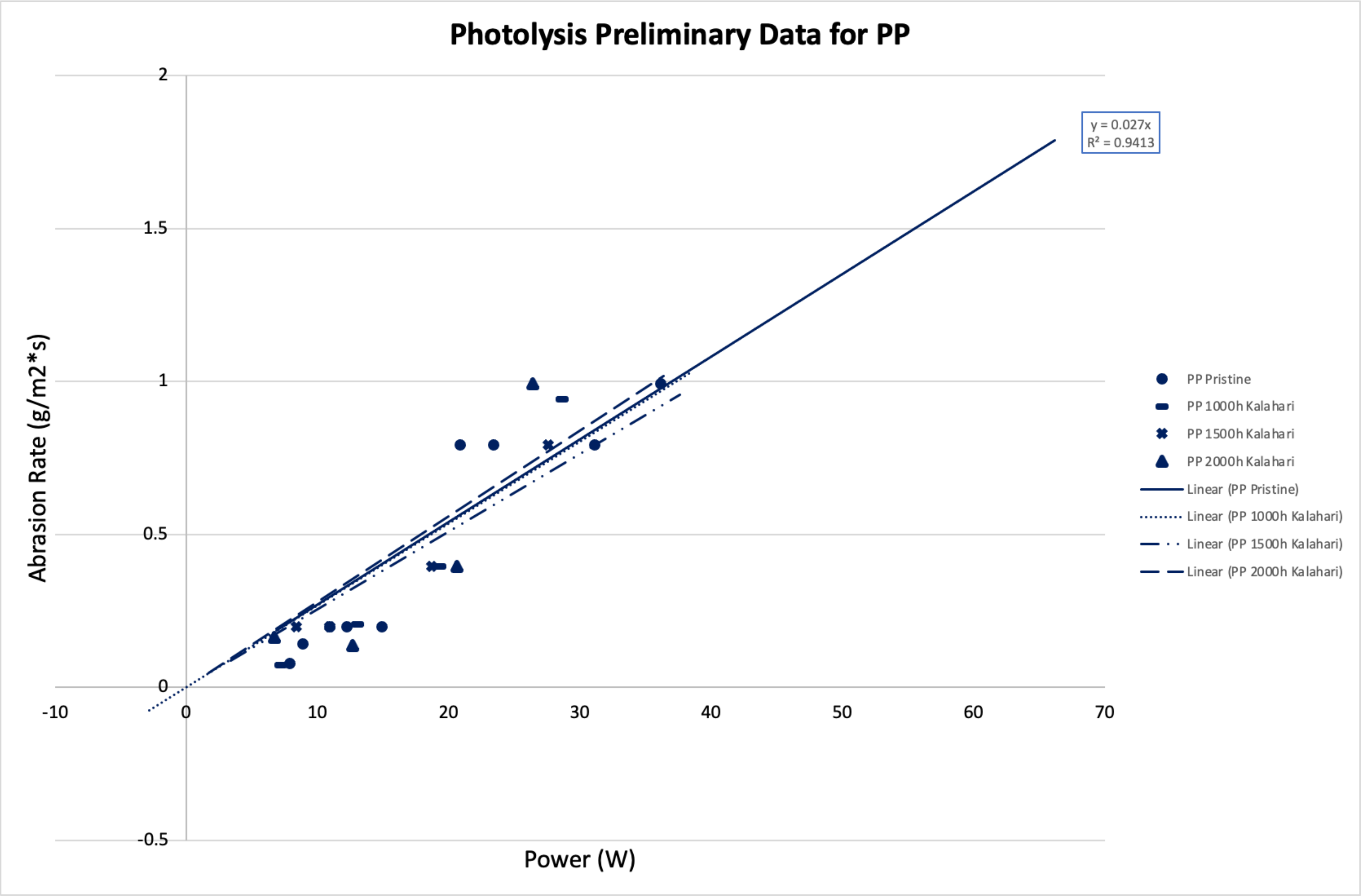
Photolysis Plastic Kalahari without replicate



Photolysis Plastic Kalahari without replicate



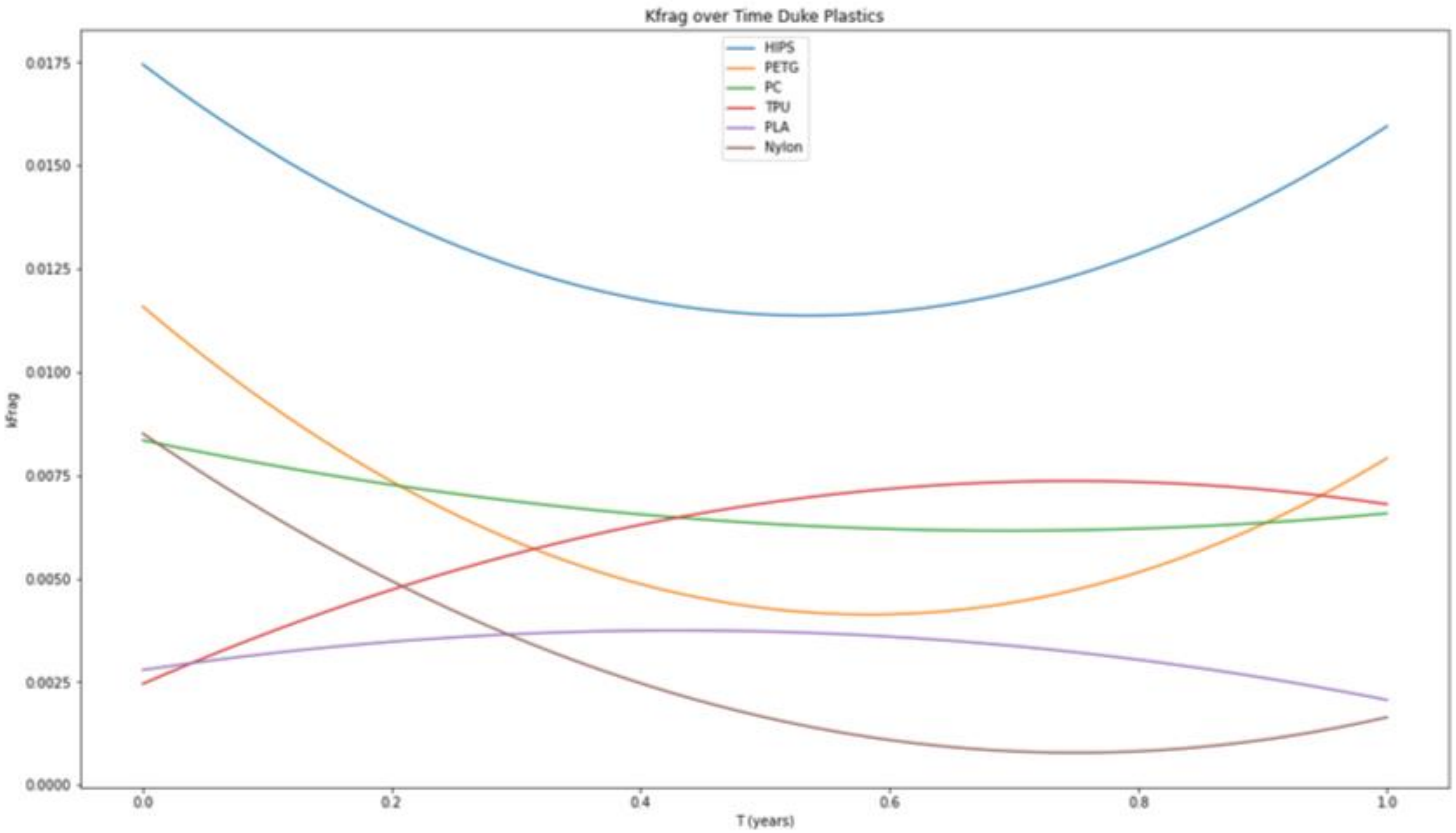
Photolysis Plastic Kalahari without replicate



Abrasion over time from Duke Plastics

K frag

$$k_{\text{frag}} = \frac{M}{\rho_c}\frac{6}{d_k}$$



HIPS Model:

$0.3646 x^2 - 0.3903 x + 0.2996$

PETG model:

$0.4486 x^2 - 0.5239 x + 0.2376$

PC model:

$0.0914 x^2 - 0.1271 x + 0.1684$

TPU model:

$-0.163 x^2 + 0.2435 x + 0.0453$

PLA model:

$-0.121 x^2 + 0.1041 x + 0.065$

$-0.005186 x^2 + 0.004461 x + 0.002786$

Nylon model:

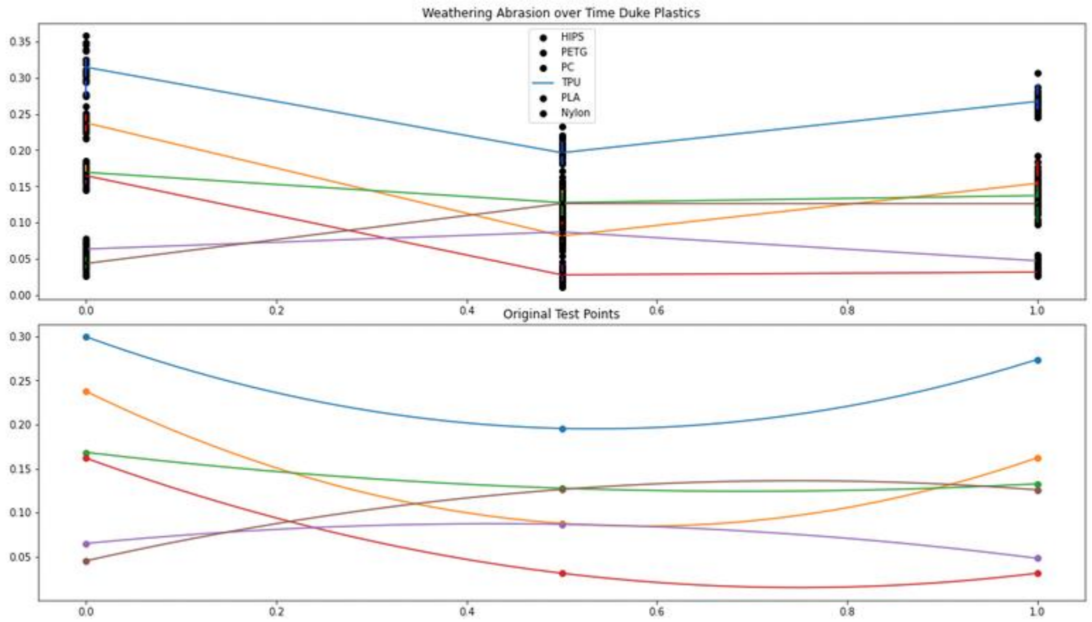
$0.2612 x^2 - 0.3918 x + 0.1618$

$0.01375 x^2 - 0.02062 x + 0.008516$

Modeling M Abrasion over Time

```
HIPS
       2
0.377 x - 0.424 x + 0.3143
PETG
        2
0.4564 x - 0.5397 x + 0.2377
PC
        2
0.1028 x - 0.1348 x + 0.1695
Nylon
        2
0.2806 x - 0.4135 x + 0.1648
PLA
         2
-0.1265 x + 0.1103 x + 0.06383
TPU
         2
-0.1654 x + 0.2479 x + 0.04387
```

```
: <matplotlib.legend.Legend at 0x2813ff160>
```



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Data integration

- ECO59 has an extension to May 2024. This will be mostly for "data integration" – taking the experimental data, applying fits/models to it and using this to produce pragmatic input requirements for end users ➞
- Also, extra timepoint in plant experiments, writing guidance and publications, and exploring integration with other projects.