Duke NICHOLAS SCHOOL OF THE ENVIRONMENT

Duke CIVIL & ENVIRONMENTAL ENGINEERING

ECO58: Comprehensive additive release and bioaccessibility model for risk assessment of micro- and nano-plastics in the environment

Project Team

Duke

P. Lee Ferguson, Ph.D.

Role: Overall PI, Lead researcher for W.P. #1, 3

Expertise and experience in polymer additive analysis and fate

Anna Lewis

Role: Graduate research assistant: W.P. #1, 3

Leaching and bioaccessibility of polymer-associated compounds in the environment

Mark R. Wiesner, Ph.D.

Role: Co-PI, Lead researcher for W.P. #2

Environmental transport modeling and Surface chemistry

Joana Sipe, Ph.D.

Role: Postdoctoral Associate: W.P. #1, 2

Quantitative modeling of polymer additive release from microplastics

Brandon Lopez

Role: Undergraduate Research Assistant: W.P. #2

Computer Science modeling of polymer additive release from microplastics

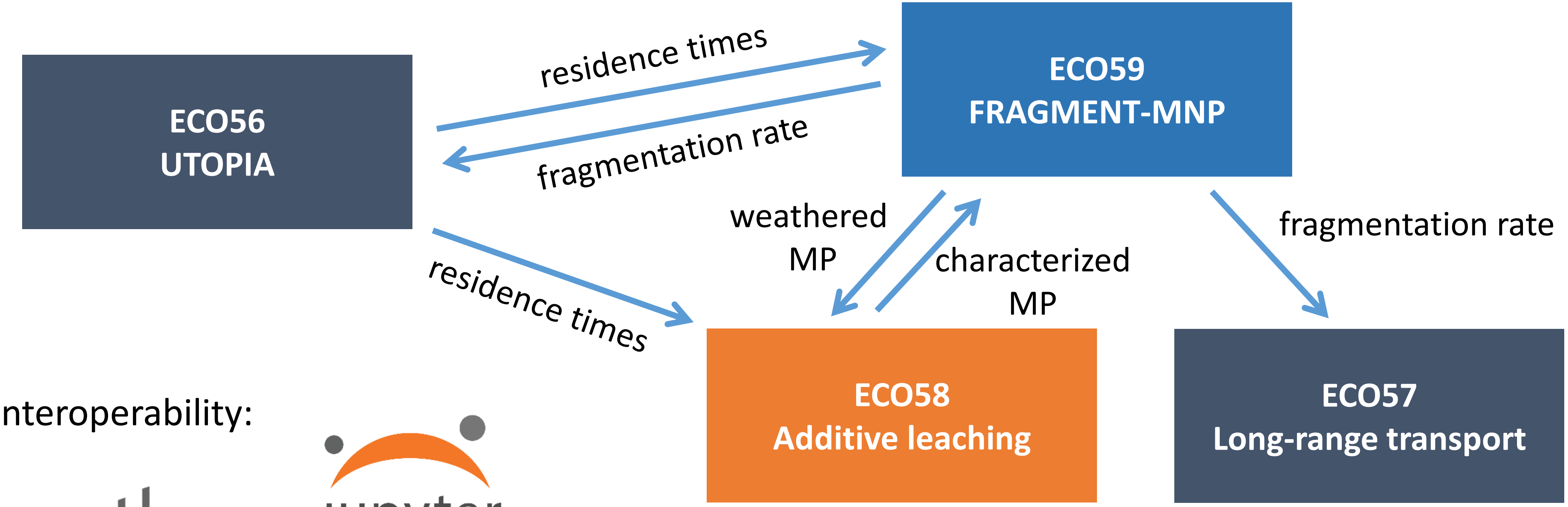
Project objectives and work packages

Objective: *Create a robust and generalizable model to predict polymer additive release, transformation (where relevant), and bioaccessibility in context of realistic aquatic environments*

This objective will be addressed through the following work packages (WP):

- **WP #1**: Compile a comprehensive literature review of polymer additive chemical space, application by polymer type, transformation, and leachability in context of ambient waters and ecological receptor ingestion.
- **WP #2**: Build and test a quantitative model to predict additive distribution among environmental compartments including polymer particles, water, and digestive environments representing deposit feeders, filter feeders, aquatic predators, and humans.
- **WP #3**: Perform laboratory-based polymer additive leaching/bioaccessibility experiments designed to parameterize, validate, and test the model built in WP# 2.

Linkages to ECO56, ECO57, and ECO59



Technical interoperability:

python jupyter

WP #1: Literature review and additive database

- Construction and utilization of a robust polymer additive release model will rely critically on the availability of high-quality input data.
- The primary output of WP#1 will be a three-element database designed to capture current knowledge associated with three data types:
  - **Data Type 1**: Additive properties, based on measured or predicted molecular/material parameters
  - **Data Type 2**: Polymer properties, based on bulk performance/manufacturing parameters of common-use and performance plastics
  - **Data Type 3**: Environmental/receptor properties, describing relevant parameters of natural waters and receptor organism gut physiology

Primary data source for Data Type 1: PlasticMap DB

Environmental Science & Technology
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Article

Deep Dive into Plastic Monomers, Additives, and Processing Aids

Helene Wiesinger,* Zhanyun Wang,* and Stefanie Hellweg

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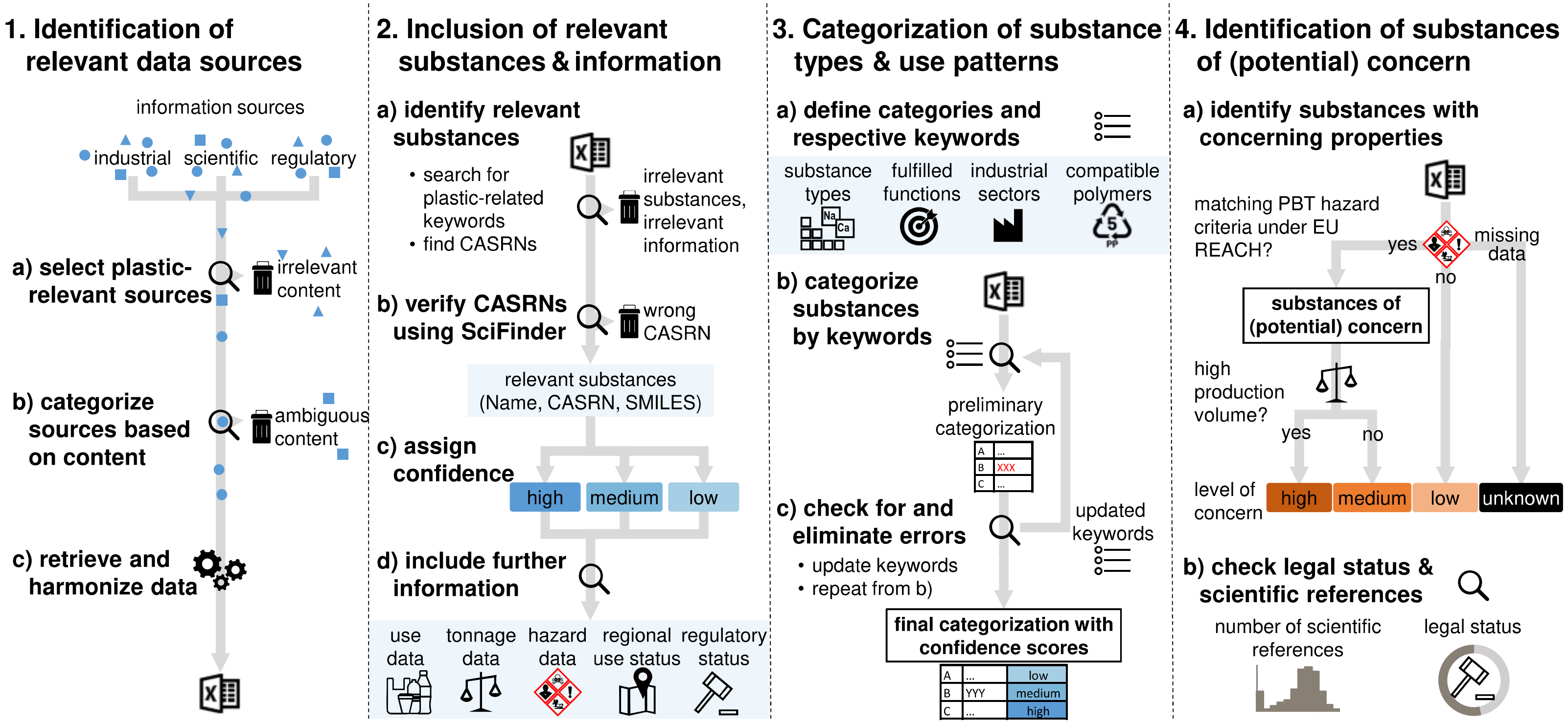
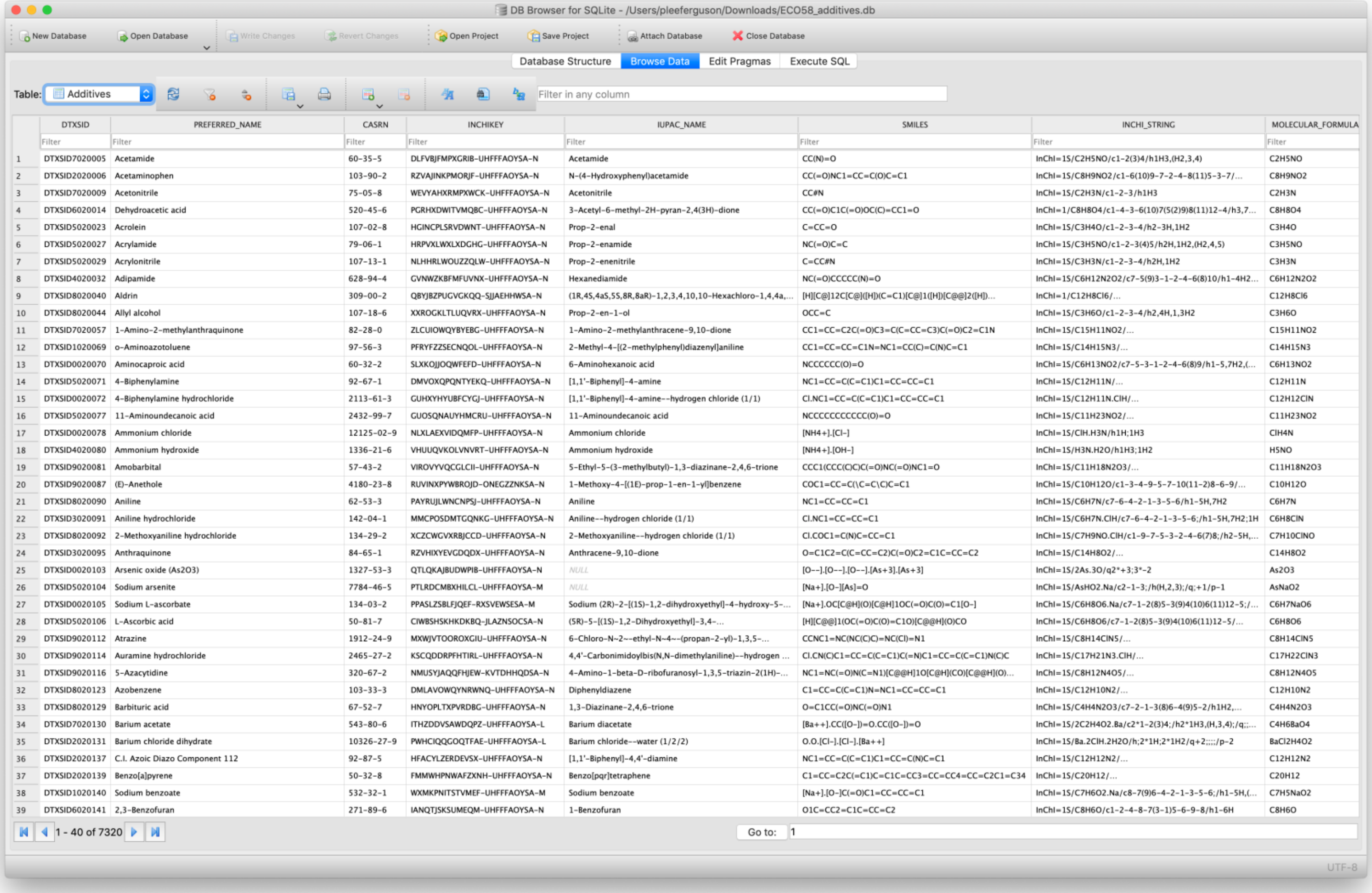


- Data sources include primary literature, prioritized regulatory lists, and trade information
- Most comprehensive molecular list of polymer-associated chemicals in existence currently
- Data available for functional use, polymer-association, production volume, etc.
- Includes ECHA Plastic Additives list (and many others)

WP #1 Deliverable: Additive DB



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	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter
1	DTXSID7020005	Acetamide	60-35-5	DLFVBJFMPXGRIB-UHFFFAOYSA-N	Acetamide	CC(N)=O	InChI=1S/C2H5NO/c1-2(3)4/h1H3,(H2,3,4)	C2H5NO
2	DTXSID2020006	Acetaminophen	103-90-2	RZVAJINKPMORJF-UHFFFAOYSA-N	N-(4-Hydroxyphenyl)acetamide	CC(=O)NC1=CC=C(O)C=C1	InChI=1S/C8H9NO2/c1-6(10)9-7-2-4-8(11)5-3-7/...	C8H9NO2
3	DTXSID7020009	Acetonitrile	75-05-8	WEVYAHXRMPXWCK-UHFFFAOYSA-N	Acetonitrile	CC#N	InChI=1S/C2H3N/c1-2-3/h1H3	C2H3N
4	DTXSID6020014	Dehydroacetic acid	520-45-6	PGRHXDWITVMQBC-UHFFFAOYSA-N	3-Acetyl-6-methyl-2H-pyran-2,4(3H)-dione	CC(=O)C1C(=O)OC(C)=CC1=O	InChI=1/C8H8O4/c1-4-3-6(10)7(5(2)9)8(11)12-4/h3,7...	C8H8O4
5	DTXSID5020023	Acrolein	107-02-8	HGINCPLSRVDWNT-UHFFFAOYSA-N	Prop-2-enal	C=CC=O	InChI=1S/C3H4O/c1-2-3-4/h2-3H,1H2	C3H4O
6	DTXSID5020027	Acrylamide	79-06-1	HRPVXLWXLXDGHG-UHFFFAOYSA-N	Prop-2-enamide	NC(=O)C=C	InChI=1S/C3H5NO/c1-2-3(4)5/h2H,1H2,(H2,4,5)	C3H5NO
7	DTXSID5020029	Acrylonitrile	107-13-1	NLHHRLWOUZZQLW-UHFFFAOYSA-N	Prop-2-enenitrile	C=CC#N	InChI=1S/C3H3N/c1-2-3-4/h2H,1H2	C3H3N
8	DTXSID4020032	Adipamide	628-94-4	GVNWZKBFMFUVNX-UHFFFAOYSA-N	Hexanediamide	NC(=O)CCCCC(N)=O	InChI=1S/C6H12N2O2/c7-5(9)3-1-2-4-6(8)10/h1-4H2...	C6H12N2O2
9	DTXSID8020040	Aldrin	309-00-2	QBYJBZPUGVGKQQ-SJJAEHHWSA-N	(1R,4S,4aS,5S,8R,8aR)-1,2,3,4,10,10-Hexachloro-1,4,4a,...	[H][C@]12C[C@]([H])(C=C1)[C@]1([H])[C@@]2([H])...	InChI=1/C12H8Cl6/...	C12H8Cl6
10	DTXSID8020044	Allyl alcohol	107-18-6	XXROGKLTLUQVRX-UHFFFAOYSA-N	Prop-2-en-1-ol	OCC=C	InChI=1S/C3H6O/c1-2-3-4/h2,4H,1,3H2	C3H6O
11	DTXSID7020057	1-Amino-2-methylanthraquinone	82-28-0	ZLCUIOWQYBYEBG-UHFFFAOYSA-N	1-Amino-2-methylanthracene-9,10-dione	CC1=CC=C2C(=O)C3=C(C=CC=C3)C(=O)C2=C1N	InChI=1S/C15H11NO2/...	C15H11NO2
12	DTXSID1020069	o-Aminoazotoluene	97-56-3	PFRYFZZSECNQOL-UHFFFAOYSA-N	2-Methyl-4-[(2-methylphenyl)diazenyl]aniline	CC1=CC=CC=C1N=NC1=CC(C)=C(N)C=C1	InChI=1S/C14H15N3/...	C14H15N3
13	DTXSID0020070	Aminocaproic acid	60-32-2	SLXKOJJOQWFEFD-UHFFFAOYSA-N	6-Aminohexanoic acid	NCCCCCC(O)=O	InChI=1S/C6H13NO2/c7-5-3-1-2-4-6(8)9/h1-5,7H2,(...	C6H13NO2
14	DTXSID5020071	4-Biphenylamine	92-67-1	DMVOXQPQNTYEKQ-UHFFFAOYSA-N	[1,1'-Biphenyl]-4-amine	NC1=CC=C(C=C1)C1=CC=CC=C1	InChI=1S/C12H11N/...	C12H11N
15	DTXSID0020072	4-Biphenylamine hydrochloride	2113-61-3	GUHXYHYUBFCYGJ-UHFFFAOYSA-N	[1,1'-Biphenyl]-4-amine--hydrogen chloride (1/1)	Cl.NC1=CC=C(C=C1)C1=CC=CC=C1	InChI=1S/C12H11N.ClH/...	C12H12ClN
16	DTXSID5020077	11-Aminoundecanoic acid	2432-99-7	GUOSQNAUYHMCRU-UHFFFAOYSA-N	11-Aminoundecanoic acid	NCCCCCCCCCCC(O)=O	InChI=1S/C11H23NO2/...	C11H23NO2
17	DTXSID0020078	Ammonium chloride	12125-02-9	NLXLAEXVIDQMFP-UHFFFAOYSA-N	Ammonium chloride	[NH4+].[Cl-]	InChI=1S/ClH.H3N/h1H;1H3	ClH4N
18	DTXSID4020080	Ammonium hydroxide	1336-21-6	VHUUQVKOLVNVRT-UHFFFAOYSA-N	Ammonium hydroxide	[NH4+].[OH-]	InChI=1S/H3N.H2O/h1H3;1H2	H5NO
19	DTXSID9020081	Amobarbital	57-43-2	VIROVYVQCGLCII-UHFFFAOYSA-N	5-Ethyl-5-(3-methylbutyl)-1,3-diazinane-2,4,6-trione	CCC1(CCC(C)C)C(=O)NC(=O)NC1=O	InChI=1S/C11H18N2O3/...	C11H18N2O3
20	DTXSID9020087	(E)-Anethole	4180-23-8	RUVINXPYWBROJD-ONEGZZNKSA-N	1-Methoxy-4-[(1E)-prop-1-en-1-yl]benzene	COC1=CC=C(\C=C\C)C=C1	InChI=1S/C10H12O/c1-3-4-9-5-7-10(11-2)8-6-9/...	C10H12O
21	DTXSID8020090	Aniline	62-53-3	PAYRUJLWNCNPSJ-UHFFFAOYSA-N	Aniline	NC1=CC=CC=C1	InChI=1S/C6H7N/c7-6-4-2-1-3-5-6/h1-5H,7H2	C6H7N
22	DTXSID3020091	Aniline hydrochloride	142-04-1	MMCPOSDMTGQNKG-UHFFFAOYSA-N	Aniline--hydrogen chloride (1/1)	Cl.NC1=CC=CC=C1	InChI=1S/C6H7N.ClH/c7-6-4-2-1-3-5-6;/h1-5H,7H2;1H	C6H8ClN
23	DTXSID8020092	2-Methoxyaniline hydrochloride	134-29-2	XCZCWGVXRBJCCD-UHFFFAOYSA-N	2-Methoxyaniline--hydrogen chloride (1/1)	Cl.COC1=C(N)C=CC=C1	InChI=1S/C7H9NO.ClH/c1-9-7-5-3-2-4-6(7)8;/h2-5H,...	C7H10ClNO
24	DTXSID3020095	Anthraquinone	84-65-1	RZVHIXYEVGDQDX-UHFFFAOYSA-N	Anthracene-9,10-dione	O=C1C2=C(C=CC=C2)C(=O)C2=C1C=CC=C2	InChI=1S/C14H8O2/...	C14H8O2
25	DTXSID0020103	Arsenic oxide (As2O3)	1327-53-3	QTLQKAJBUDWPIB-UHFFFAOYSA-N	NULL	[O--].[O--].[O--].[As+3].[As+3]	InChI=1S/2As.3O/q2*+3;3*-2	As2O3
26	DTXSID5020104	Sodium arsenite	7784-46-5	PTLRDCMBXHILCL-UHFFFAOYSA-M	NULL	[Na+].[O-][As]=O	InChI=1S/AsHO2.Na/c2-1-3;/h(H,2,3);/q;+1/p-1	AsNaO2
27	DTXSID0020105	Sodium L-ascorbate	134-03-2	PPASLZSBLFJQEF-RXSVEWSESA-M	Sodium (2R)-2-[(1S)-1,2-dihydroxyethyl]-4-hydroxy-5-...	[Na+].OC[C@H](O)[C@H]1OC(=O)C(O)=C1[O-]	InChI=1S/C6H8O6.Na/c7-1-2(8)5-3(9)4(10)6(11)12-5;/...	C6H7NaO6
28	DTXSID5020106	L-Ascorbic acid	50-81-7	CIWBSHSKHKDKBQ-JLAZNSOCSA-N	(5R)-5-[(1S)-1,2-Dihydroxyethyl]-3,4-...	[H][C@@]1(OC(=O)C(O)=C1O)[C@@H](O)CO	InChI=1S/C6H8O6/c7-1-2(8)5-3(9)4(10)6(11)12-5/...	C6H8O6
29	DTXSID9020112	Atrazine	1912-24-9	MXWJVTOOROXGIU-UHFFFAOYSA-N	6-Chloro-N~2~-ethyl-N~4~-(propan-2-yl)-1,3,5-...	CCNC1=NC(NC(C)C)=NC(Cl)=N1	InChI=1S/C8H14ClN5/...	C8H14ClN5
30	DTXSID9020114	Auramine hydrochloride	2465-27-2	KSCQDDRPFHTIRL-UHFFFAOYSA-N	4,4'-Carbonimidoylbis(N,N-dimethylaniline)--hydrogen ...	Cl.CN(C)C1=CC=C(C=C1)C(=N)C1=CC=C(C=C1)N(C)C	InChI=1S/C17H21N3.ClH/...	C17H22ClN3
31	DTXSID9020116	5-Azacytidine	320-67-2	NMUSYJAQQFHJEW-KVTDHHQDSA-N	4-Amino-1-beta-D-ribofuranosyl-1,3,5-triazin-2(1H)-...	NC1=NC(=O)N(C=N1)[C@@H]1O[C@H](CO)[C@@H](O)...	InChI=1S/C8H12N4O5/...	C8H12N4O5
32	DTXSID8020123	Azobenzene	103-33-3	DMLAVOWQYNRWNQ-UHFFFAOYSA-N	Diphenyldiazene	C1=CC=C(C=C1)N=NC1=CC=CC=C1	InChI=1S/C12H10N2/...	C12H10N2
33	DTXSID8020129	Barbituric acid	67-52-7	HNYOPLTXPVRDBG-UHFFFAOYSA-N	1,3-Diazinane-2,4,6-trione	O=C1CC(=O)NC(=O)N1	InChI=1S/C4H4N2O3/c7-2-1-3(8)6-4(9)5-2/h1H2,...	C4H4N2O3
34	DTXSID7020130	Barium acetate	543-80-6	ITHZDDVSAWDQPZ-UHFFFAOYSA-L	Barium diacetate	[Ba++].CC([O-])=O.CC([O-])=O	InChI=1S/2C2H4O2.Ba/c2*1-2(3)4;/h2*1H3,(H,3,4);/q;;...	C4H6BaO4
35	DTXSID2020131	Barium chloride dihydrate	10326-27-9	PWHCIQQGOQTFAE-UHFFFAOYSA-L	Barium chloride--water (1/2/2)	O.O.[Cl-].[Cl-].[Ba++]	InChI=1S/Ba.2ClH.2H2O/h;2*1H;2*1H2/q+2;;;;/p-2	BaCl2H4O2
36	DTXSID2020137	C.I. Azoic Diazo Component 112	92-87-5	HFACYLZERDEVSX-UHFFFAOYSA-N	[1,1'-Biphenyl]-4,4'-diamine	NC1=CC=C(C=C1)C1=CC=C(N)C=C1	InChI=1S/C12H12N2/...	C12H12N2
37	DTXSID2020139	Benzo[a]pyrene	50-32-8	FMMWHPNWAFZXNH-UHFFFAOYSA-N	Benzo[pqr]tetraphene	C1=CC=C2C(=C1)C=C1C=CC3=CC=CC4=CC=C2C1=C34	InChI=1S/C20H12/...	C20H12
38	DTXSID1020140	Sodium benzoate	532-32-1	WXMKPNITSTVMEF-UHFFFAOYSA-M	Sodium benzoate	[Na+].[O-]C(=O)C1=CC=CC=C1	InChI=1S/C7H6O2.Na/c8-7(9)6-4-2-1-3-5-6;/h1-5H,(...	C7H5NaO2
39	DTXSID6020141	2,3-Benzofuran	271-89-6	IANQTJSKSUMEQM-UHFFFAOYSA-N	1-Benzofuran	O1C=CC2=C1C=CC=C2	InChI=1S/C8H6O/c1-2-4-8-7(3-1)5-6-9-8/h1-6H	C8H6O

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Journal of Cheminformatics

RESEARCH ARTICLE Open Access

OPERA models for predicting physicochemical properties and environmental fate endpoints

Kamel Mansouri[1,2,3*], Chris M. Grulke[1], Richard S. Judson[1] and Antony J. Williams[1]

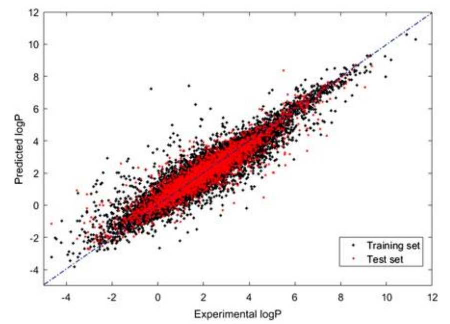


Fig. 6 Experimental and predicted values for training and test set of OPERA logP model

Collaborators at US EPA:

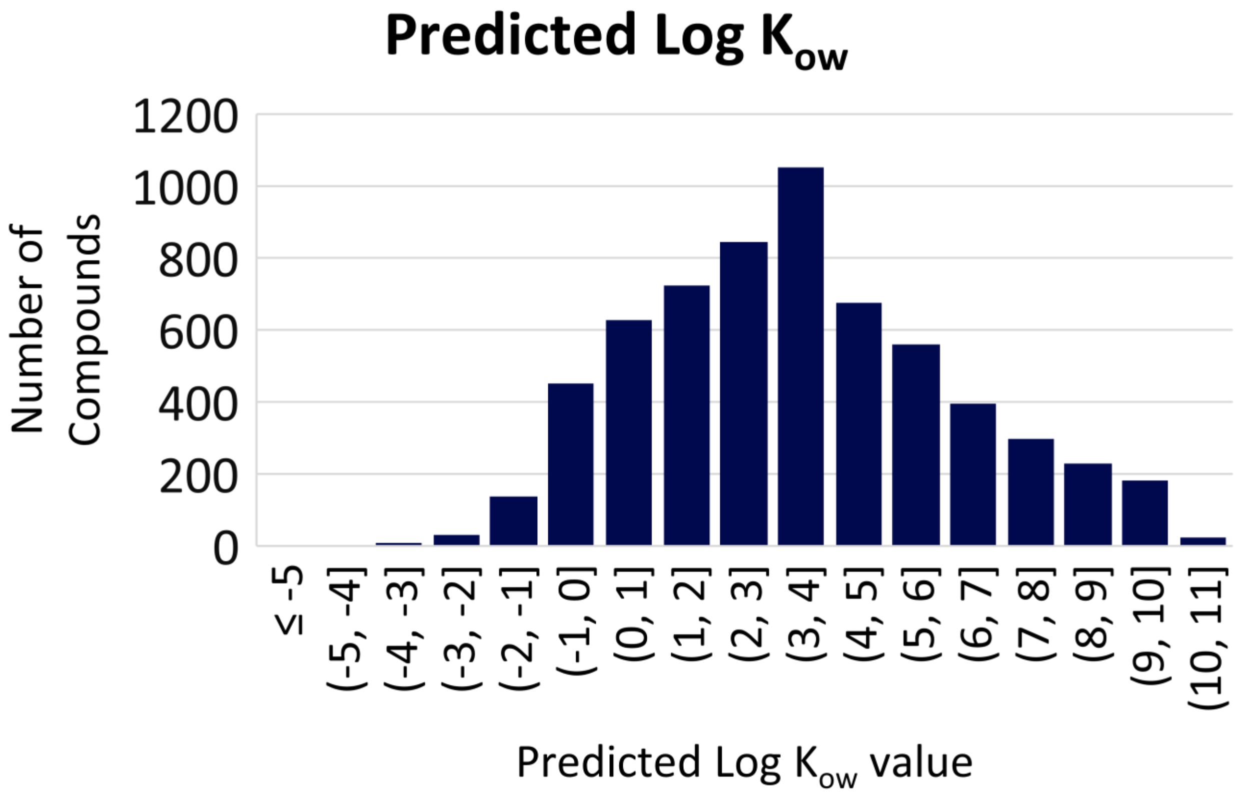
Dr. Antony Williams

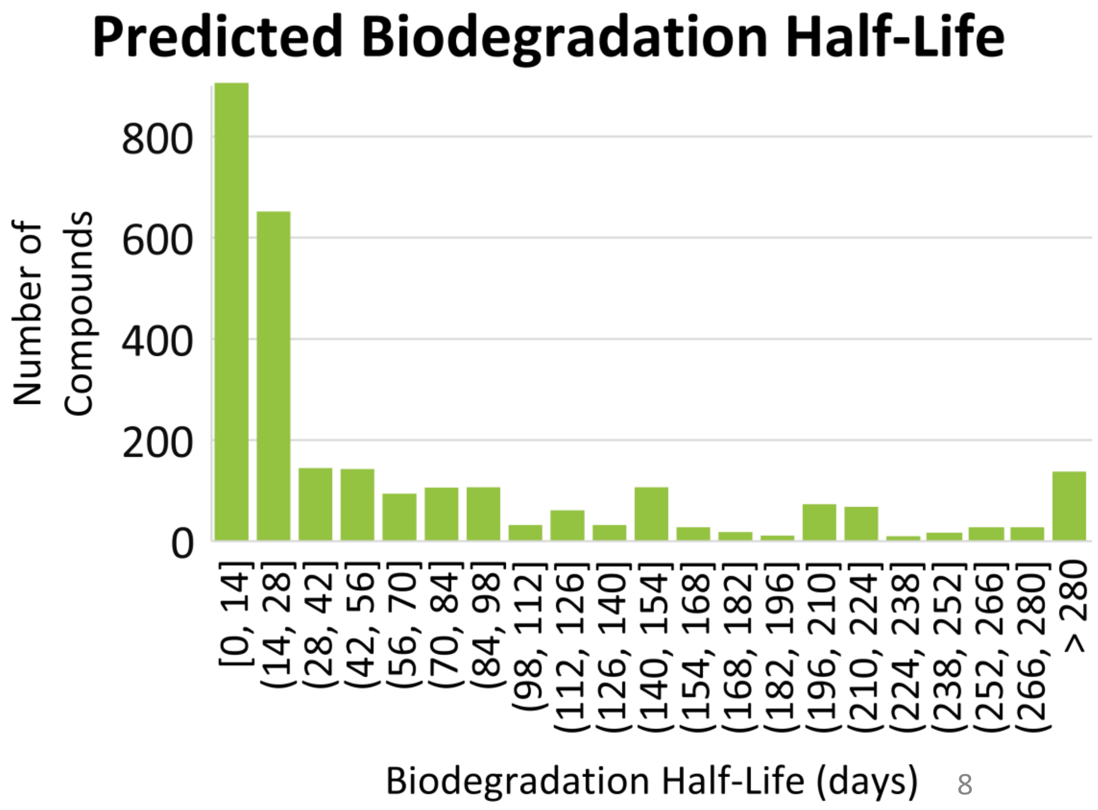
Dr. Charles Lowe

OPERA model predictions for > 6200 compounds yielding physicochemical properties e.g. solubility, log K_{ow}, biodegradation half life, etc.

WP #1 Deliverable: Additive DB

OPERA model predictions for > 6200 compounds yielding physicochemical properties e.g. solubility, log K_{ow}, biodegradation half life, etc.

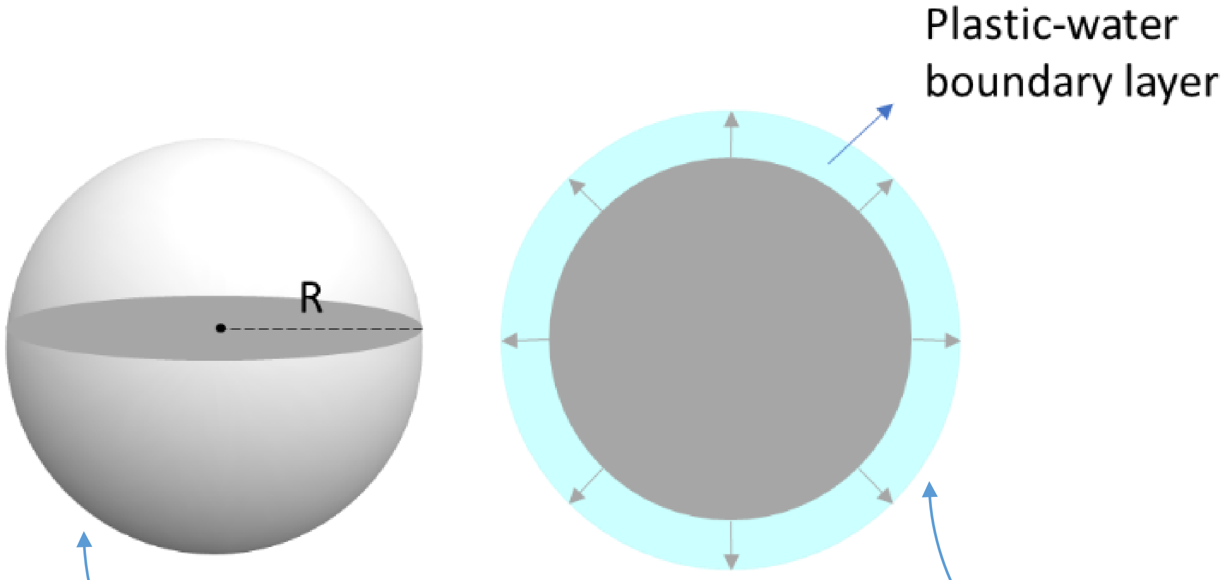




WP #2: Additive release model development and testing

- Mathematical formulation for several cases:
  - Non-reactive additives (analytical and numerical)
  - Reactive additives and pertinent degradation reactions (numerical)
  - **Non-homogeneous distribution within fragments (numerical)**
- The primary outputs of WP#2 will be an “instance”- based structure for interfacing with data collection and a numerical code that can be integrated as a subroutine in a larger particle- population model for particulate plastics.
- Calculations of additive release in a variety of “media” including:
  - **Release into water using Fick’s model**
  - Ocean water
  - Atmospheric water
  - Representative vertebrate “gut” environments

WP #2: Additive release model development and testing



Diffusion within plastic fragment

$$\frac{\partial q}{\partial t} = \frac{D_S}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial q}{\partial r}\right) \pm RXNs$$

$$\frac{\partial C}{\partial t} + \vec{v} \cdot \nabla C = k(C - C_S) - k_{phot}C - k_{hdr}C \pm RXNs$$

Transport into fluid through boundary layer and reactions

Modeling Release of Additive

```python
def Mt_mo(Dp, n2,  t, r, Bi, a=1):
    #might need a fitting coefficient which would be a
    if bi <= 0:
        test = a * Dp*t*(r)**-2
    elif 1 < Bi < 100:
        test = n2*(Dp*t*R**-2)**.5
    else:
        x = np.linspace(1, t+1, t+1)
        test = np.array([(6/((pi)**2))*nsum(
            lambda x: (1/x**2)*exp(-(x**2)*(pi**2)*((Dp*t)/(R**2))),[1,inf]) for t in range(t+1)])
    return test
```

$$\frac{M_q}{M_\infty} = \exp\left(-\frac{D_w}{K_{pw}\delta L_c}t\right) \qquad (10)$$

Table 1. Summarized analytical solutions of remaining mass fraction of additives inside plastics under three situations.

Case	Expression of F	Parameters			
Case I	$F=\sum_{n=1}^{\infty} B_n \exp(-A_n^2 \cdot Fo)$		A_n	B_n	
		Flat	$(2n+1)\pi$	$2/A_n^2$	
		Cylinder	$R_c\alpha_n$	$4/A_n^2$	
		Sphere	$n\pi$	$6/A_n^2$	
Case II	$F=\sum_{n=1}^{\infty} \frac{A\exp(-\beta_n{}^2 Fo)}{B_n}$		A_n	B_n	β_n
		Flat	$2Bi^2$	$\beta_n^2(\beta_n^2+Bi^2 - Bi)$	$\beta_n \tan\beta_n - Bi = 0$
		Cylinder	$4Bi^2$	$\beta_n^2(\beta_n^2+Bi^2)$	$\beta_n J_1[\beta_n] - Bi J_0[\beta_n] = 0$
		Sphere	$6Bi^2$	$\beta_n^2(\beta_n^2+Bi^2 + Bi)$	$\beta_n \cot\beta_n + Bi - 1 = 0$
Case III	$F=\exp(-Bi\cdot Fo)$				

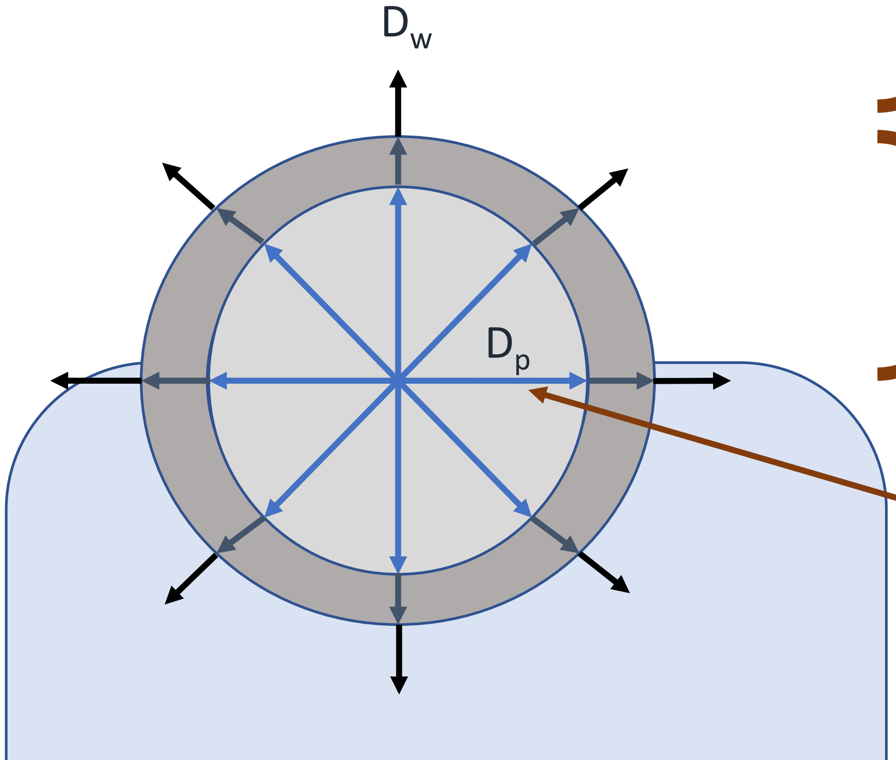
Use Diffusion rate in leachate

Use Bi # out of plastic or from surface. Usually case 3

Blue Arrows- Internal Plastic Diffusion

Gray Arrows – Microplastic Surface Boundary Layer

Black Arrows – Diffusion in water



Rate limiting step additive out of microplastic

Plot Additive Release into Leachate

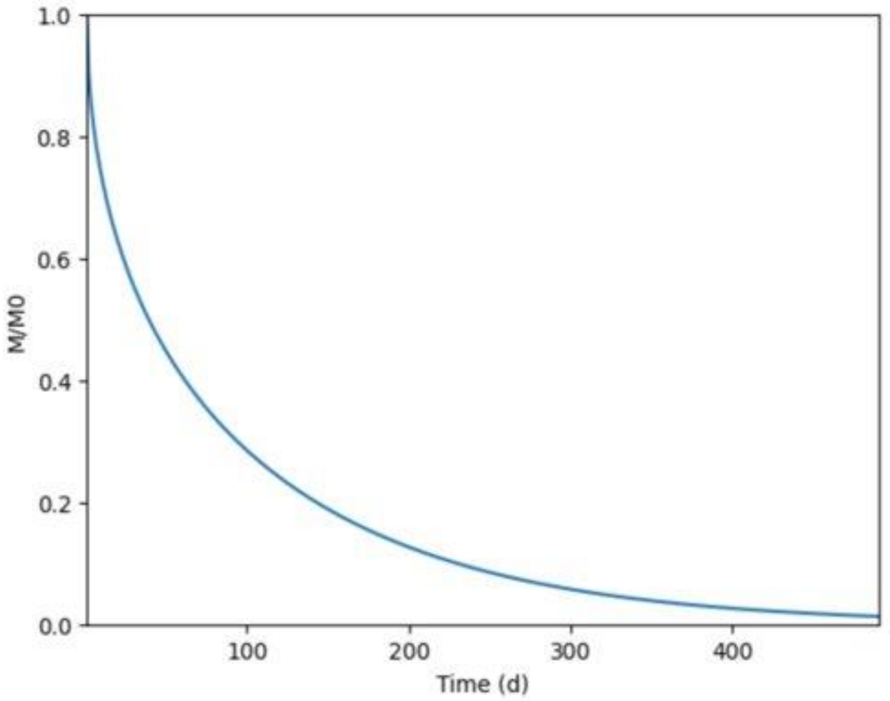
```
def Biot_number(Dp, R, Dw, Kpw, S):
    k = mass_transfer(Dw, Kpw, S)
    B = (k*R)/(Dp)
    return B

#Has to be adjusted for each solution
def mass_transfer(Dw, Kpw, S):
    k = Dw/(Kpw*S)
    return k

def M_inf(Dp,t,k,R, n2, a=1):
    global c
    Dp=float(Dp)
    t = int(t)
    k = float(k)
    R=float(R)
    Bi = k*R/ Dp
    print("Bi = " + str(Bi))
    x = np.linspace(1, t+1, t+1)
    test = np.array([(6/((pi)**2))*nsum(
        lambda x: (1/x**2)*exp(-(x**2)*(pi**2)*((Dp*t)/(R**2))),[1,inf]) for t in range(t+1)])
    plt.ylim(0,1)
    plt.margins(0)
    plt.plot(x,test)
    plt.xlabel("Time (d)")
    plt.ylabel("M/M0")
```

```
print(Dp)
print(K)
print(R)
M_inf(dp.value, time.value, k.value, r.value)
```

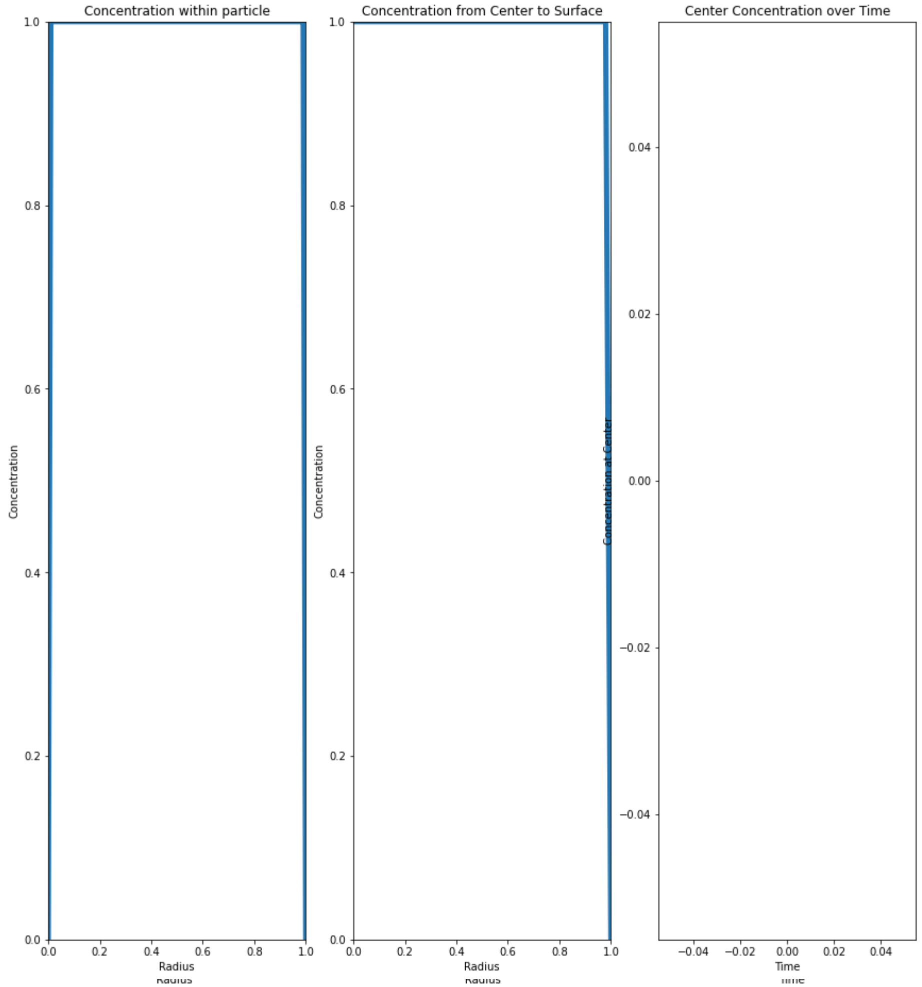
```
5e-12
13.0
5e-05
Bi = 25000000.0
```



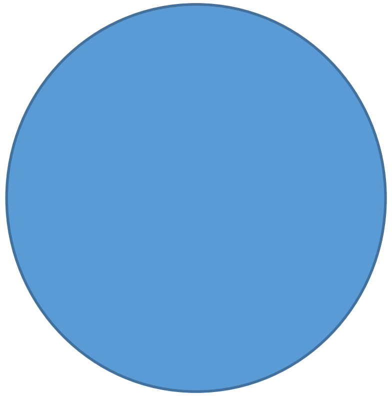
Numerical solution: Homogeneous initial distribution

```
diffusion(100, 1, 1, 0)

Concentration at the Center 1.0
Concentration right before reaching the Surface 1.0
Average concentration throughout particle 1
```



Particle: blue is additive



WP #3: Additive leaching and bioaccessibility experiments

- Testing, ground-truthing, and parameterization of the additive release model will require comparison with experimental data.
- Experiments in WP #3 will be designed to explore:
  - Influence of additive chemical structure on leachability (QSAR approach)
  - Polymer type/geometry/chemistry as a driving factor for leachability
  - Impact of type and extent of weathering (e.g. physical vs. chemical vs. photolytic) on additive leaching
  - Additive localization on/in polymer and its influence on leaching
  - Gut digestive fluid parameters and their importance to additive leaching from polymers
  - Reactivity and transformation of leachable additives

Selection of polymer candidates for leaching experiments

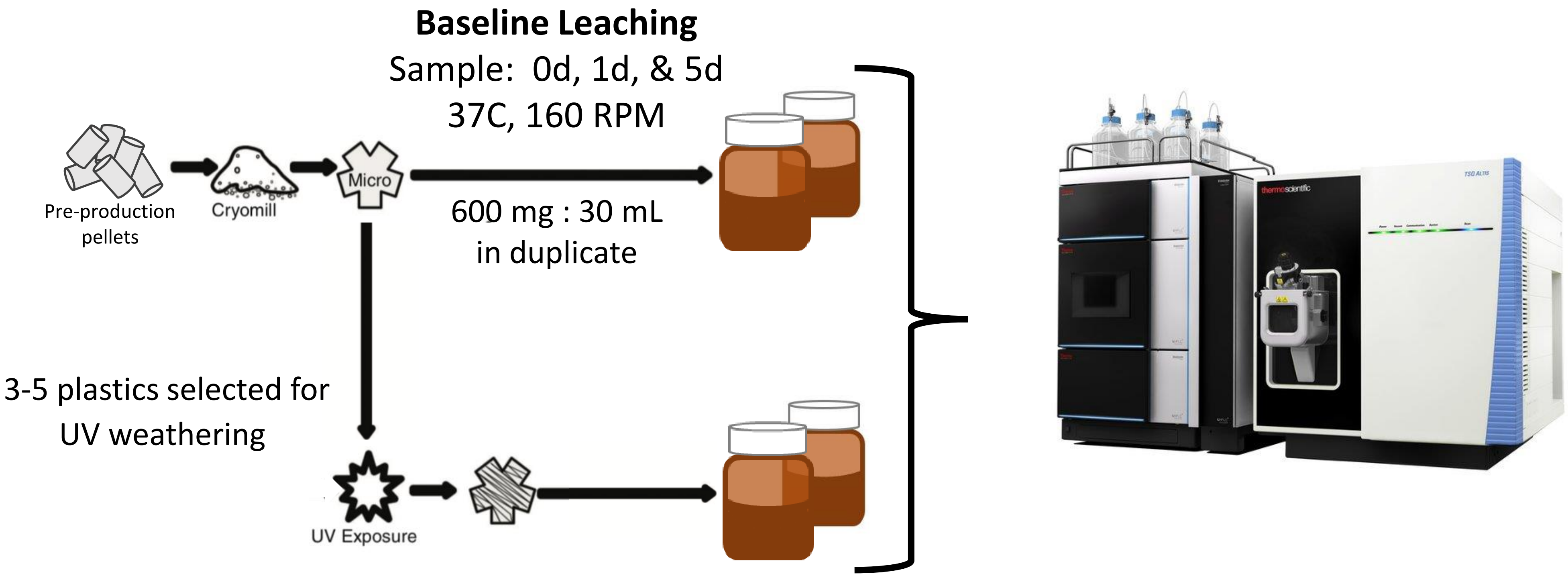
Source	Polymer Type- long name	Abbrev.	Form
NIST Polymer Kit 1.0	Ultra low-density polyethylene	ULDPE	pellet
	Low-density polyethylene	LDPE.1	pellet
	Low-density polyethylene	LDPE.2	pellet
	Linear low-density polyethylene	LLDPE.1	pellet
	Linear low-density polyethylene made with metallocene catalyst	LLDPE.2	pellet
	Medium-density polyethylene	MDPE	pellet
	High-density polyethylene	HDPE.1	pellet
	High-density polyethylene	HDPE.2	pellet
	Polypropylene	PP	pellet
	Polyester poplin fabric	PEST	fabric coupon
	Polyethylene terephthalate	PET.1	pellet
	Recycled polyethylene terephthalate	PET.2	pellet
	20% Ethylene-vinyl acetate	EVA	pellet
	Acrylonitrile- butadiene-styrene	ABS	pellet
	Expanded polystyrene foam	EPS	foam bead
	Polystyrene	PS	pellet, powder
	Nylon 6	PA6	pellet, powder
	Nylon 6,6	PA66	pellet, powder
	Polyvinyl chloride	PVC.1	pellet
	Polyvinyl chloride with phthalates	PVC.2	pellet
	Crumb rubber from used tires	CR	crumbed particle
	Cellulose acetate	CA	powder

Source	Polymer Type- long name	Abbrev.	Form
NIST SRM	Low-density polyethylene	LDPE	pellet
	High-density polyethylene	HDPE II	pellet
	High-density polyethylene	HDPE III	pellet
via ECO59 Team	High-impact polystyrene	HIPS	powder
	Nylon 6		powder
	Thermoplastic polyurethane	TPU	powder
	Polylactic acid	PLA	powder
	Low-density polyethylene	LDPE	powder
	Polypropylene	PP	powder
	Polyethylene terephthalate	PET	powder
Goodfellow via Millipore Sigma; filament spool	Polyethylene terephthalate filament (clear)	PET	sliced fibers
Amazon; water-repellant fleece jacket	Polyester fibers (black)	PES	sheared fibers
Chinese Fabric store; thread spool	Polyester thread (green)	PES	sliced fibers
Home-Furnishing store; couch sleeve	Polyester fabric (blue)	PES	cryomilled powder

Examples of experimental conditions available for testing in leaching experiments

Additive Type	• Surface-coating (e.g. PFAS components for stain resistance/water-repellency) • Intrinsic additive (e.g. disperse azobenzene dyes in polyester microfibers) • Performance additive (e.g. antioxidants such as Antioxidant 168 or UV inhibitors such as HALS)
Polymer Type	• Polyolefin (relatively inert to direct UV degradation, e.g. polypropylene) • Aromatic thermoplastic (glassy and UV-active, e.g. polystyrene) • Elastomer (rubbery and subject to oxidation, e.g. polyurethane)
Weathering Treatment	• UV exposure (pre-treatment of polymer with SUNTEST XLS+ in laboratory) • Physical abrasion/fragmentation (laboratory abrader or cryomill) • Oxidant exposure (pre-treatment with ozone or peroxide)
Leaching Treatment	• Water (fresh-to-brackish, pH 5-8, dissolved organic matter, temperature 4º - 40º C) • Simulated or actual digestive fluid (bile salt surfactants, lipase, pepsin, other enzymes, pH 2-7)

Example experimental design for laboratory leaching experiments



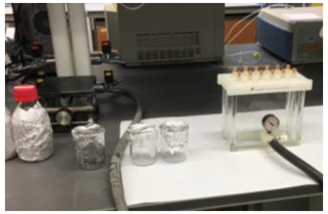
Identification and quantitation by liquid chromatography tandem mass spectrometry

Adapted from: Walker, I. et al., *Environ. Chem.* 2021, **18**, 131–141

Sample Type

Polymer

Leachates & digestates



Processing

- Cryomill to microplastics
- Solvent extraction

- Solid-phase extraction for digestate cleanup
- Filtration and direct-injection of water leachates where possible

Analysis

- UPLC – HRMS/MS
- Acetonitrile and water w/ 0.1% formic acid
- Thermo Fisher Orbitrap Fusion Lumos Mass Spectrometer
  - Data dependent MS/MS
  - Critical resolution (500,000)
  - Mass accuracy < 1 ppm
  - ESI +/- ionization

Structure Annotation

- Compound Discover 3.2™
- Feature Consolidation of CD results
- Spectral library matching
  - MzCloud, MONA, NIST
  - 75% or greater match

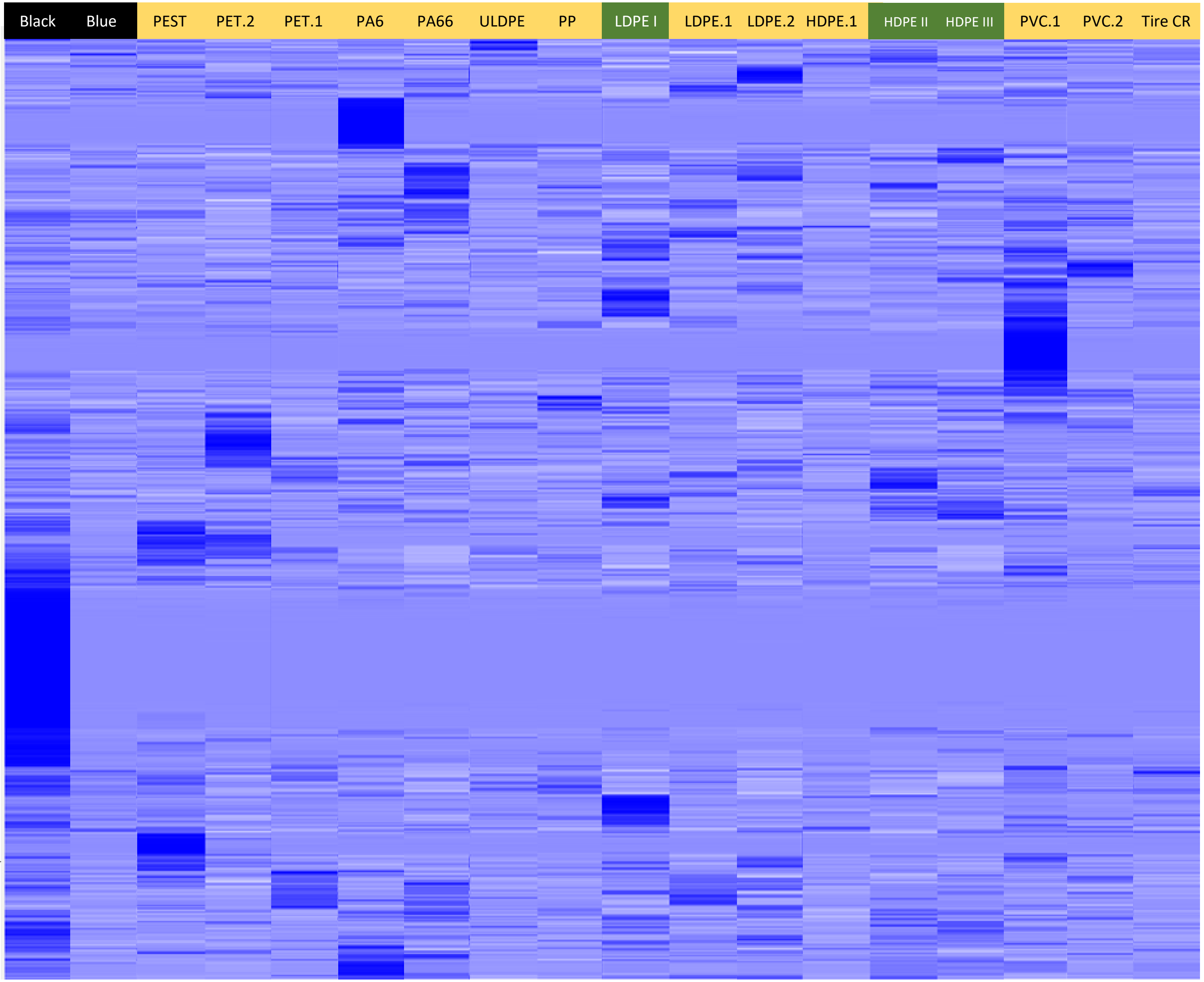
- *In Silico* MS/MS prediction
  - Sirius (molecular formula)
  - CSI-FingerID
- Definitive identification from > 30 in house polymer associated chemical standards

Additive Characterization of Polymer Extracts: ESI (+)

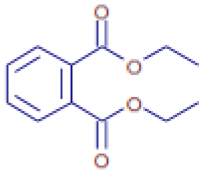
Source

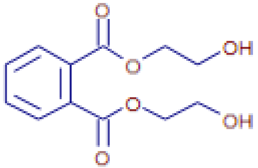
- NIST Polymer Kit 1.0
- NIST SRM
- Commercial Polyesters

Polymer



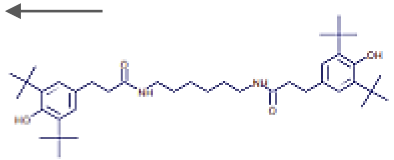
Diethyl Phthalate





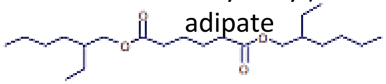
Bis(2-hydroxyethyl) phthalate

AO 1098

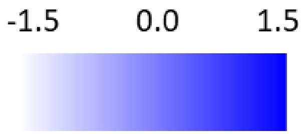


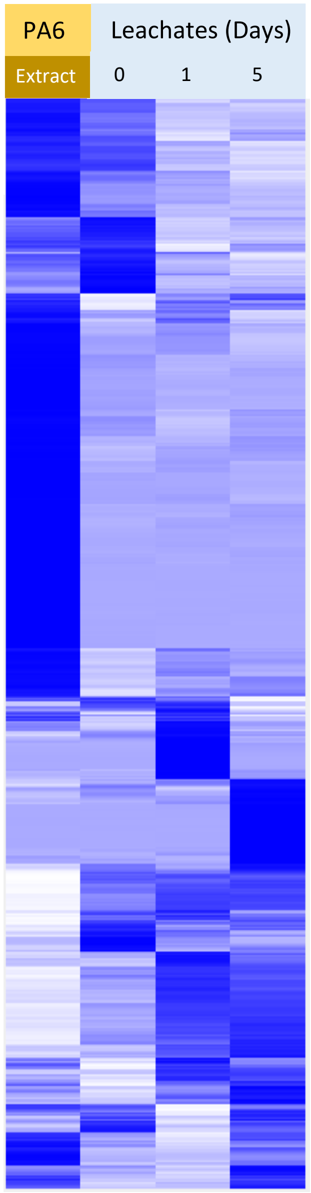
PEGn

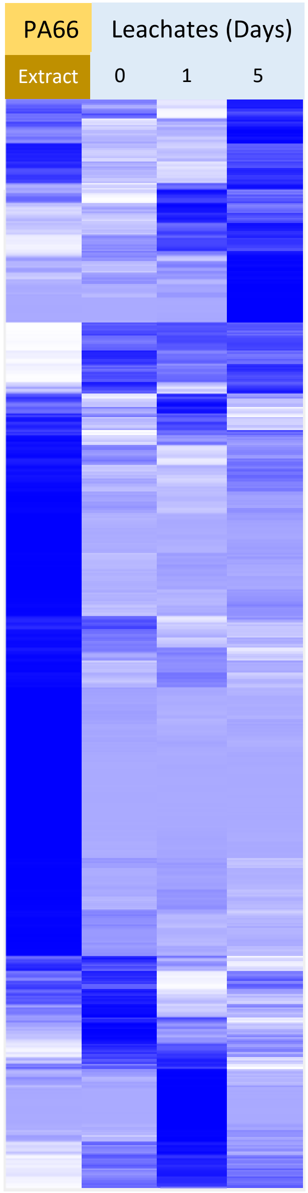
Bis(2-ethylhexyl) adipate

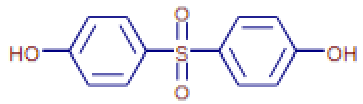


Polymer Kit 1.0 Nylons: PA6 and PA66

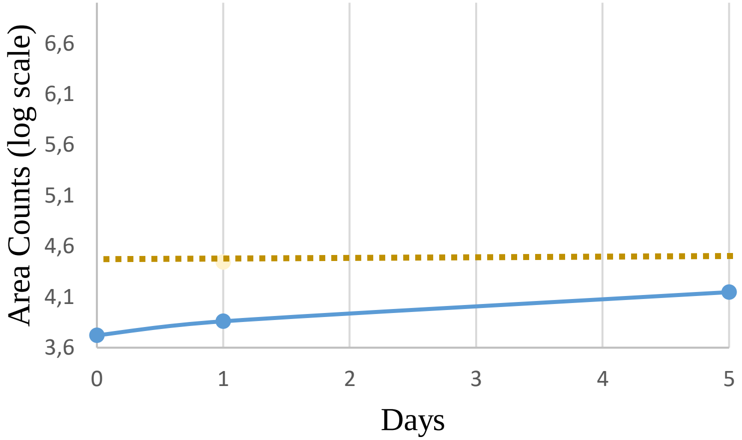




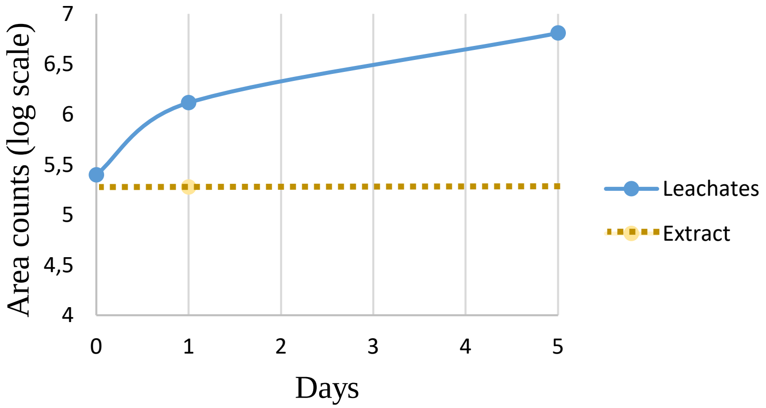


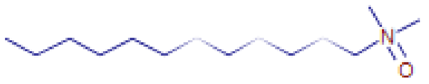


PA66: **Bisphenol S**



PA6: N,N-Dimethyldodecylamine N-oxide





Confirmed by standard

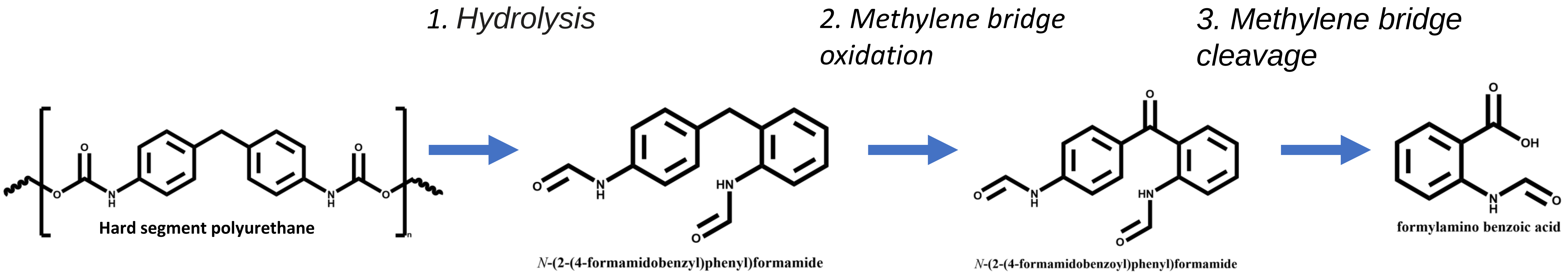
vs

Probable Identification

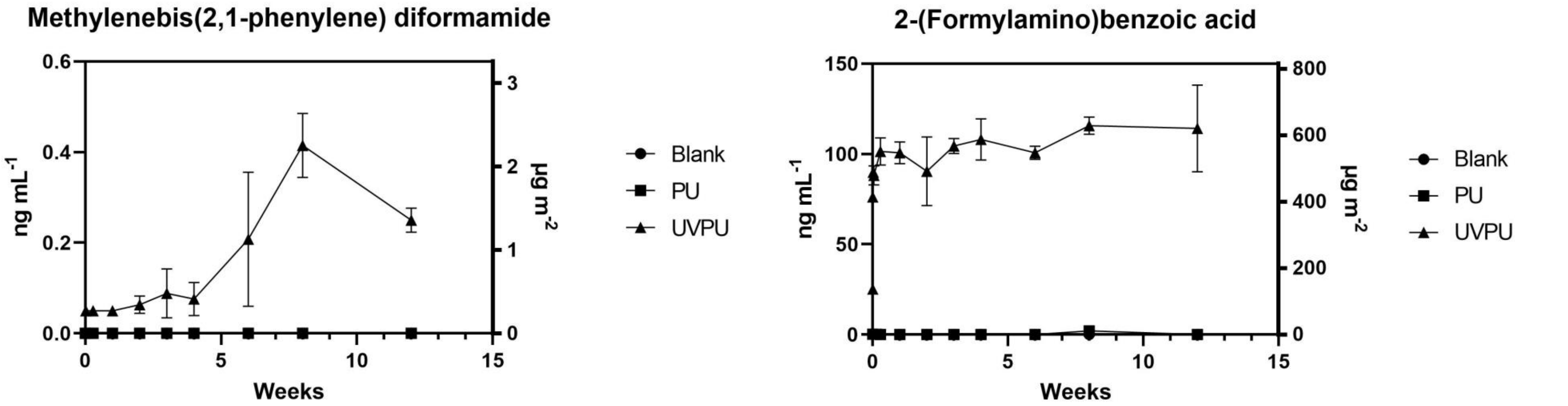
Experimental plan for laboratory leaching experiments

Materials	Experiment	Completion
NIST Polymer Kit 1.0 and SRM pellets	Cryogenically mill to powder for experimentation	✓
All 36 representative polymers (50 mg of each)	Accelerated solvent extraction (ASE)	✓
All representative polymers except 7 ECO59 plastics (600 mg of each in duplicate)	Baseline Water leaching experiment (37˚C, 160 rpm) EPA moderately hard water	✓
Extracts and water-leachates of all representative polymers and ECO59 hydrolysis experiment samples	Characterization of polymer additive content via suspect screening non-target analysis	✓ ECO59 plastics: June 2023
Select polymers (3-5) to undergo UV weathering	Subject to UV exposure (12d, 500 Watt/m^2) and conduct ASE and 24-hr leaching experiments	May 2023
Select polymers (4-8) for additive diffusion rate determination in select biological and environmental fluids (2-4)	48-hr Additive leaching experiment (timepoints: 0, 2, 4, 8, 16, 24, 48)	July 2023

Example results: Release of polyurethane degradation products after UV exposure



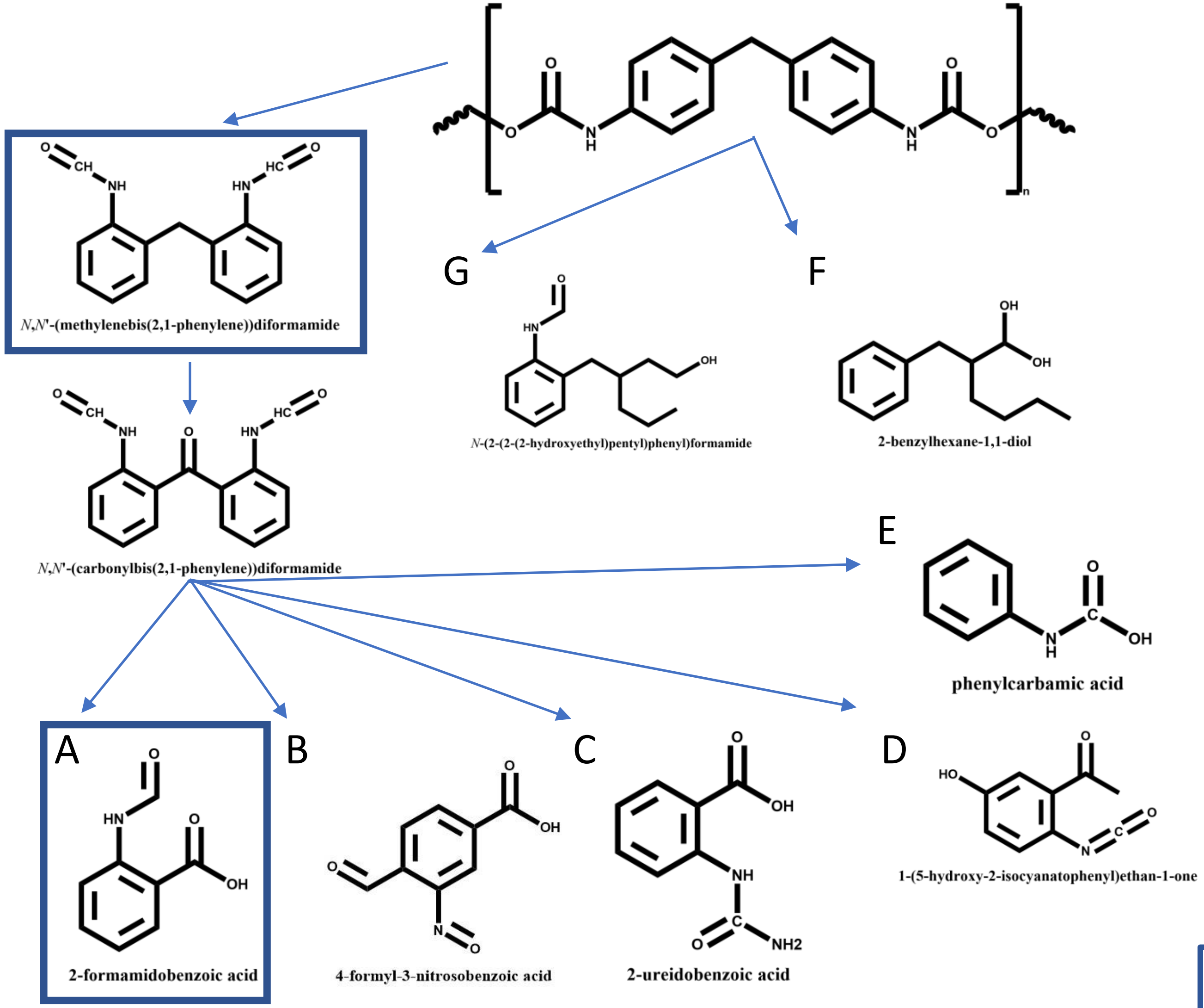
Laboratory Controlled Leaching

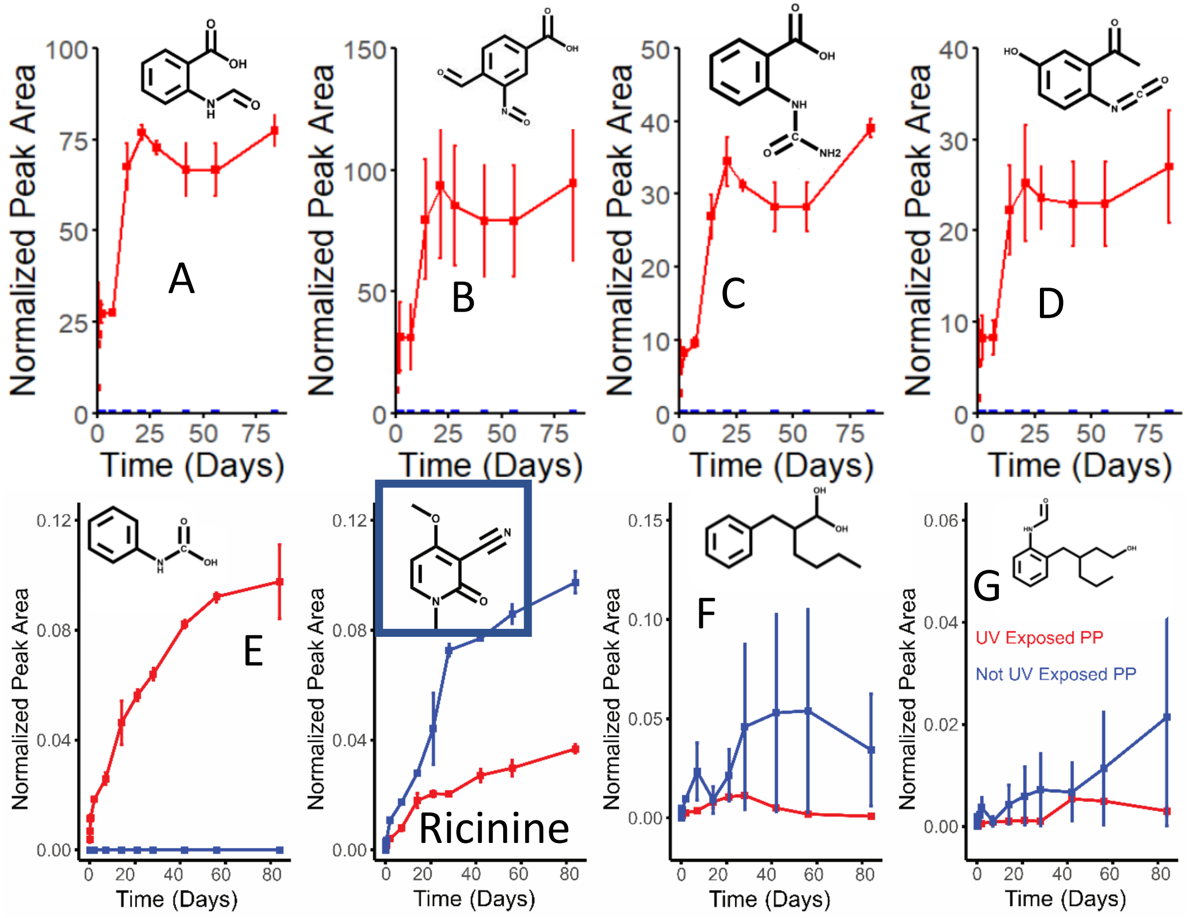


- UV light degrades the hard segments of the polymer structure
- Hydrolysis and oxidation products are leachable into water

Data from Dr. Imari Walker-Franklin (Ph.D. Dissertation, 2021)

Example results: Release of polyurethane degradation products after UV exposure



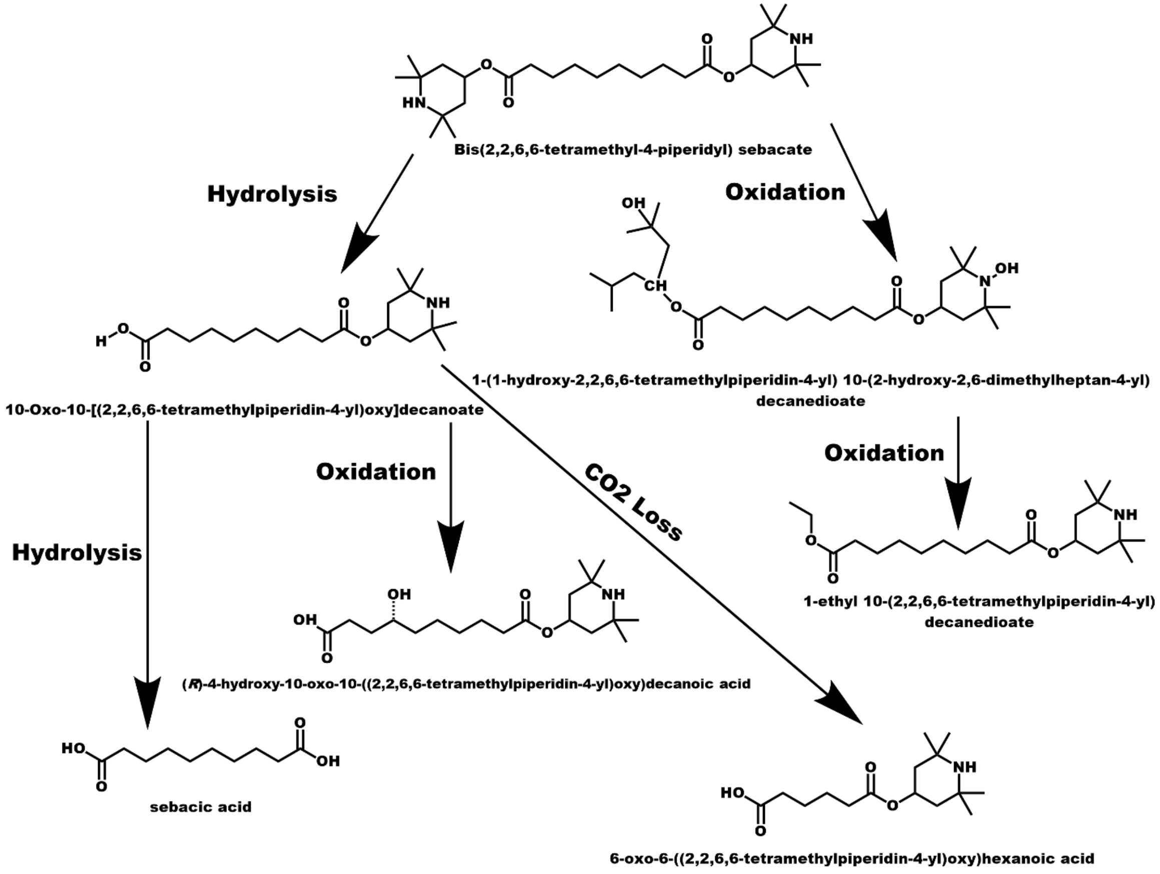


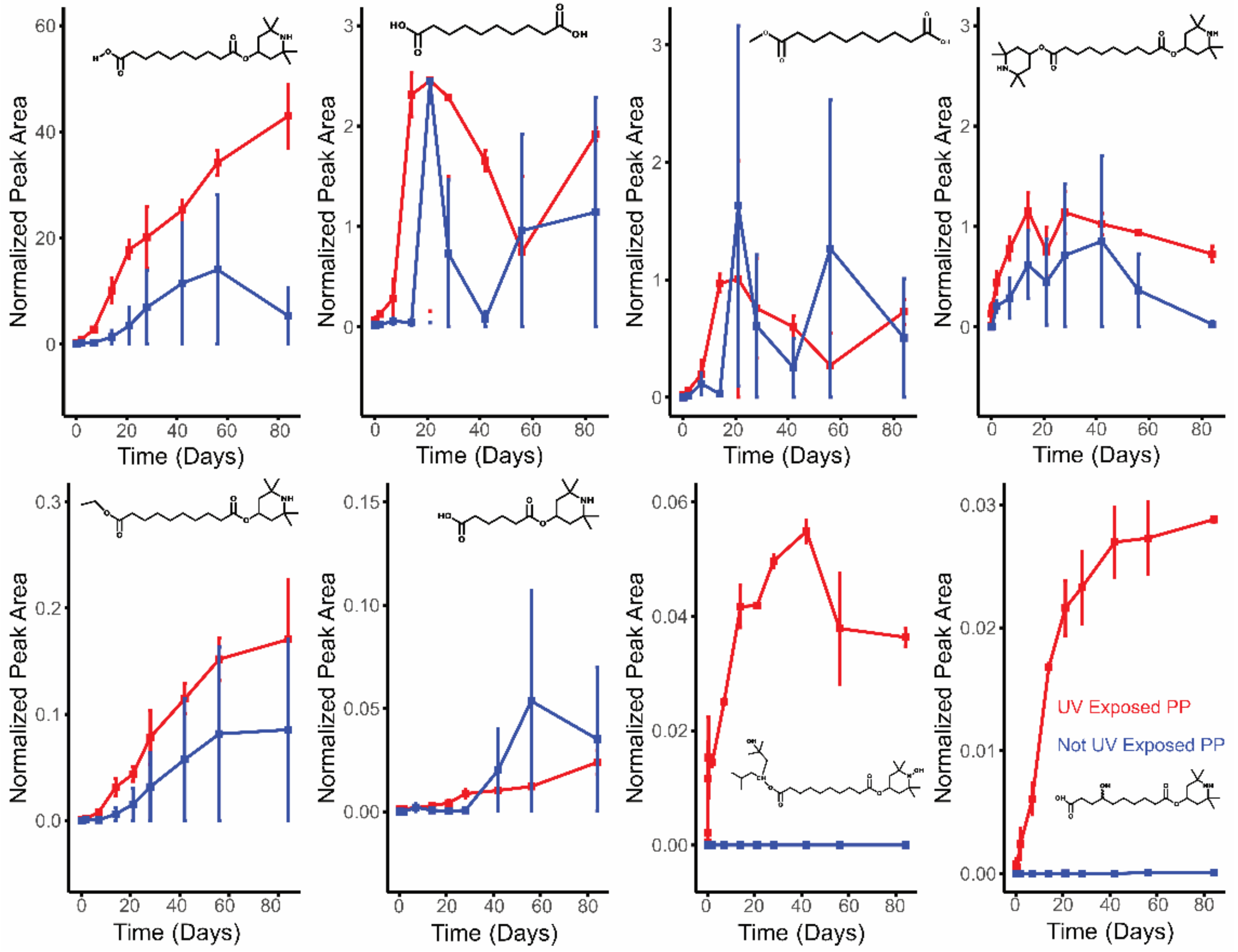
*Compounds confirmed by standard

Data from Dr. Imari Walker-Franklin (Ph.D. Dissertation, 2021)

Example results: Additive leaching and bioaccessibility experiments

Example results: Release and transformation of hindered amine light stabilizer from weathered polypropylene





Data from Dr. Imari Walker-Franklin (Ph.D. Dissertation, 2021)

Anticipated leaching study parameterization in WP #3

- We anticipate testing a matrix of polymer, additive, and leaching/bioaccessiblity conditions including:
  1. 3-5 microplastic polymer sizes/types (e.g. PET microfibers vs. abraded PVC microparticles)
  2. At least two polymer weathering treatments (e.g. UV-pretreated & fragmented vs. untreated & fragmented)
  3. At least two leaching/bioaccessibility solutions (e.g. simulated deposit-feeder digestive fluid vs. simulated lake water)
- Polymers, additives, and leaching experimental conditions will be decided after completion of WP #1 (literature review) and during WP #2 (model development) for maximum impact and utility.

Discussion and next steps

Polymer additive database metrics

Molecular additive database:

- Current size:
  - 7,320 unique substances (compiled from 10,547 substances in PlasticMAP & other)
  - 7,102 compounds with InChIKey
- Database annotations and connections:
  - CASRN
  - Molecular identifiers including InChI and InChIKey
  - Substance classifications
  - Functional use and polymer-association (facile link to Data Type #2)
  - Publication, patent, ToxCast assay counts
  - Production volume
- NEW physicochemical property predictions:
  - 6,200 compounds predicted
  - Molecular properties include solubility, vapor pressure, K_{ow}, K_{oa}, pK_a, bioconcentration factor

Leaching media properties and conditions

Digestive environments		Feeding strategy	Digestive system chemistry	Temperature	pH	Contact angle
Low trophic level: Invertebrate	Mollusc	Suspension- feeder	Enzymatic	18- 24 °C	5.9 – 8	
	Polychaete	Deposit- feeder	Surfactant	18- 24 °C	6.74 - 7.8	44 - 52
Mid trophic level: Cold-blooded vertebrate	Fish	Predator	Acidic pH	18- 24 °C	2 - 5	
High trophic level: Warm-blooded vertebrate	Seabird	Predator	Acidic pH	38- 40 °C	4.7	
	Human	Predator	Gastric (acidic pH) & Intestinal	37 °C	1.5 & 7	
Biological fluids		**Exposure route**	**Media chemistry**	**Temperature**	**pH**	**Contact angle**
	Sweat	Dermal	Acidic pH	40 °C	4.7	
	Lung	Inhalation	Surfactant	37 °C	4.5	
Ambient waters		**Ionic strength (mol L^{-1})**	**DOM (mg C L^{-1})**	**Temperature**	**pH**	**Contact angle**
	Seawater	0.7	<1	18- 20 °C	8.2	87 -91
	Freshwater	0.02	0.5 - 20	23- 27 °C	7.4 – 7.8	

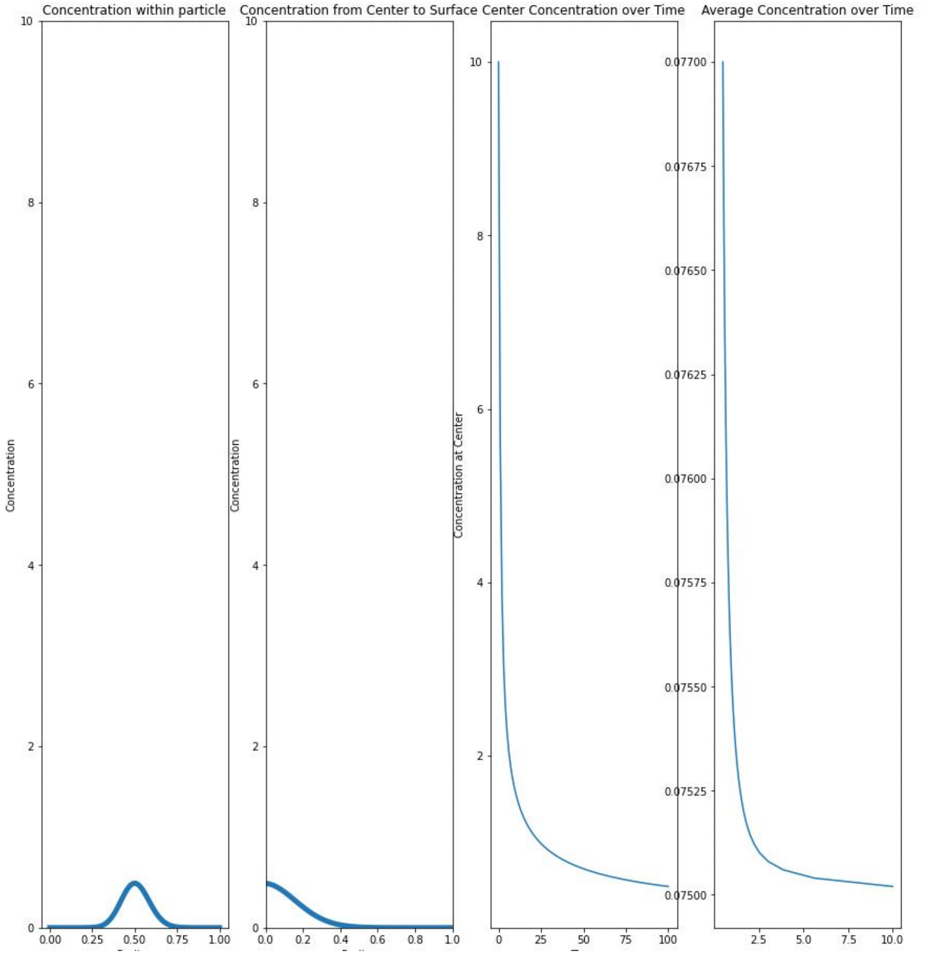
Products of WP #1

- Primary database containing all three data types (molecules, polymers, and environmental/receptor properties):
  - Useful as input for model developed in WP #2
  - Will help identify gaps in knowledge to be filled in WP #3
  - Extremely valuable resource for non-targeted analysis of polymer additives in the environment (future work)
  - **STATUS**: Complete
- Comprehensive review/analysis manuscript for publication
  - Objective: Publish the most comprehensive treatment to-date on polymer additives and their release into environmental media
  - Target: High-impact journal in the field of environmental science (e.g. *Environmental Science & Technology*)

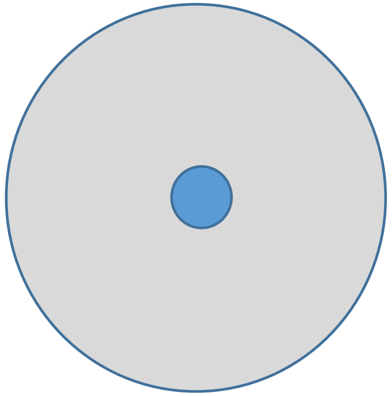
Numerical solution: Center initial distribution

```
diffusion(100, 10, 1, 100)

Average concentration at center  0.014676657270909116
Concentration at the Center 0.4892219090303038
Concentration right before reaching the Surface 2.6056551456399825e-07
Average concentration throughout particle 0.07699997664780367
```



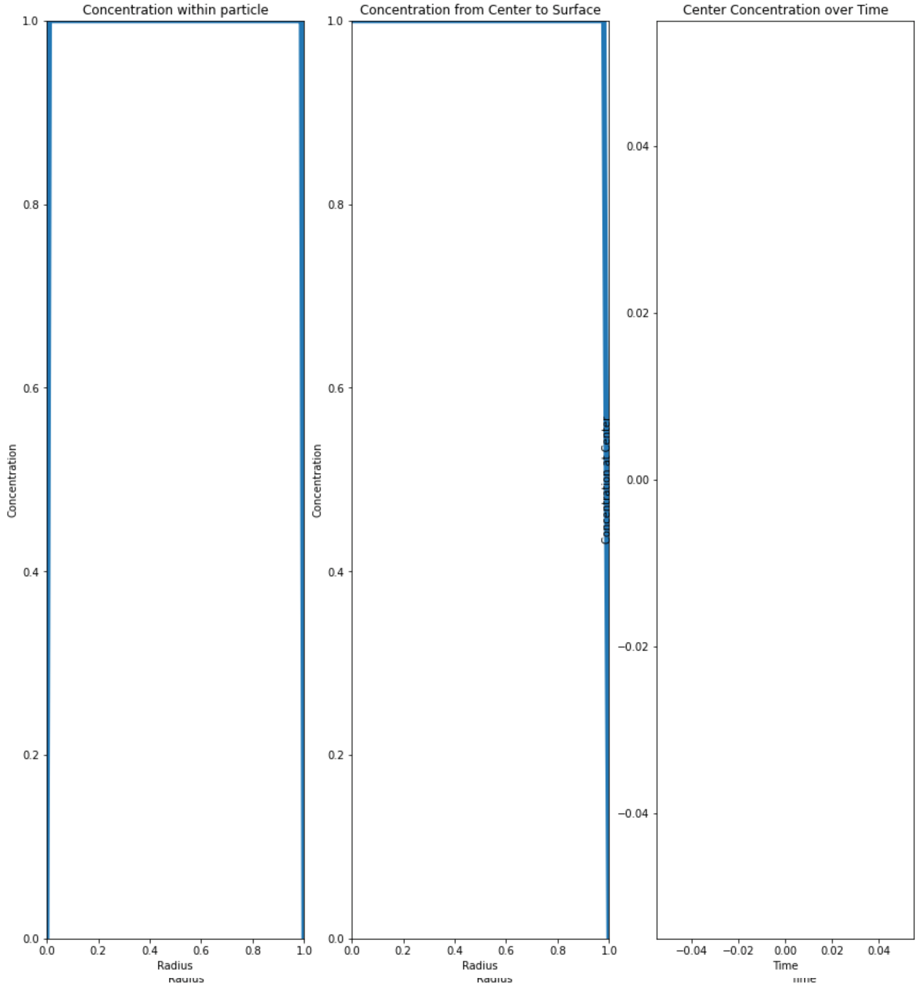
Particle: blue is additive



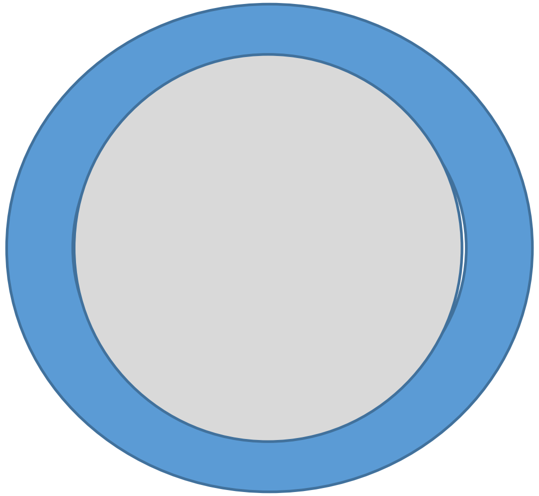
Numerical solution: Surface initial distribution

```
diffusion(100, 1, 1, 0)
```

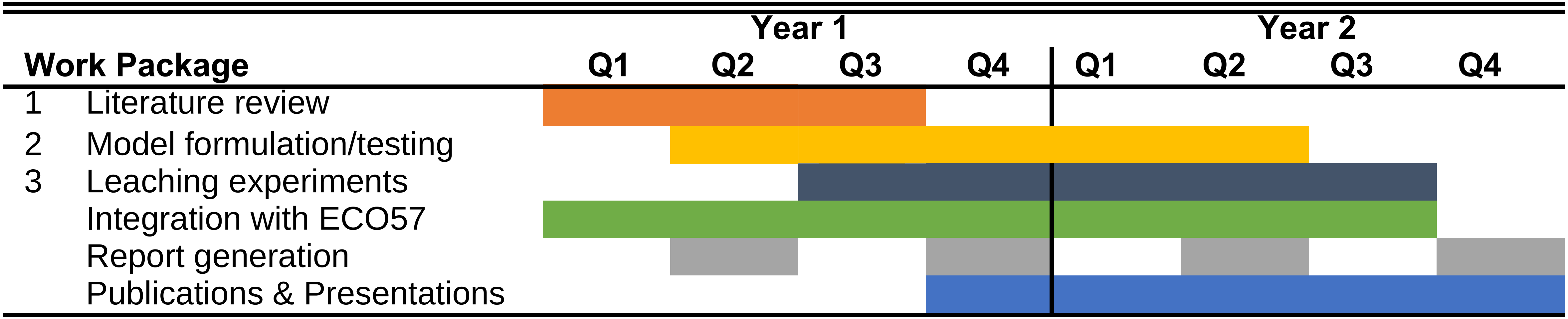
```
Concentration at the Center 1.0
Concentration right before reaching the Surface 1.0
Average concentration throughout particle 1
```



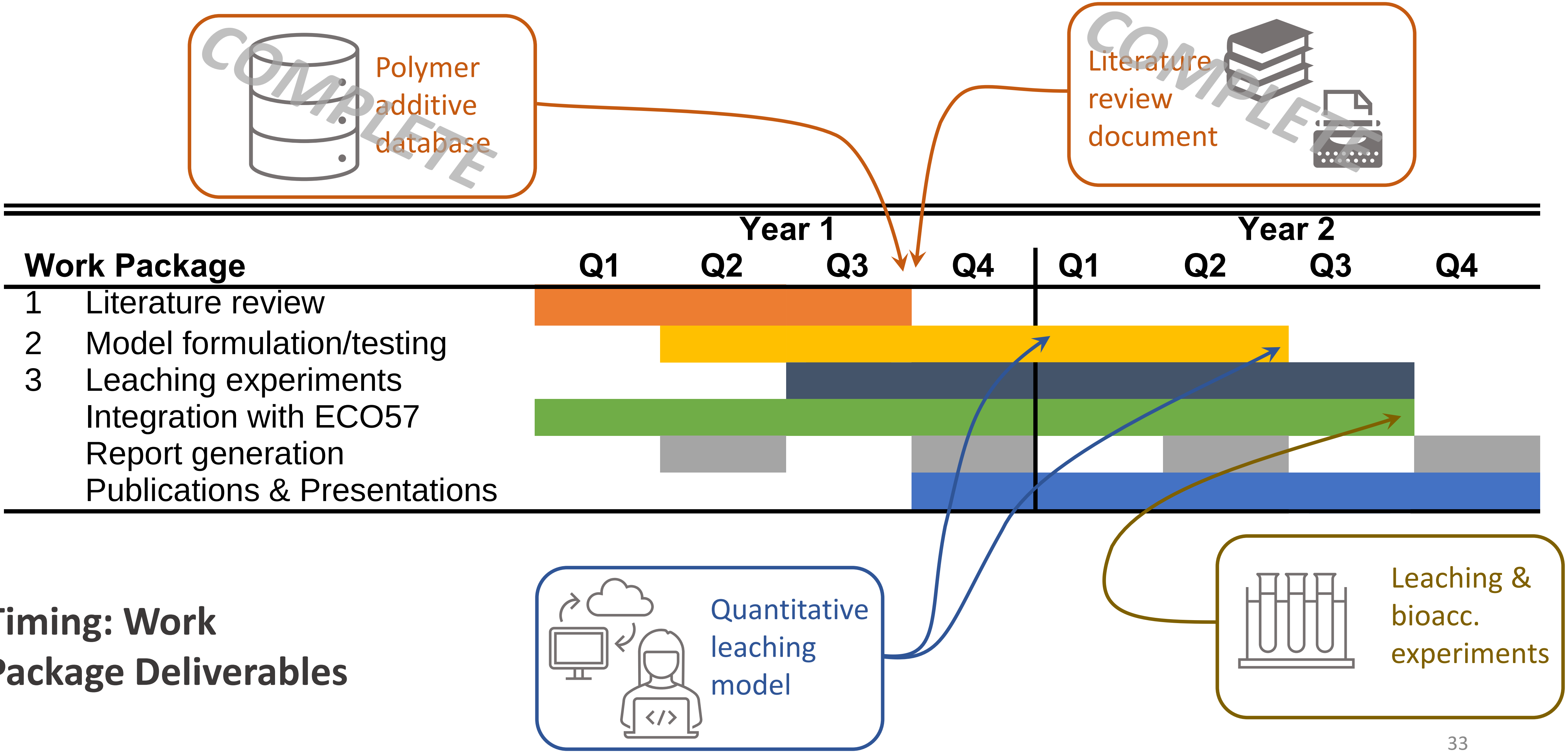
Particle: blue is additive



Project Timeline



Project Timeline



Timing: Work Package Deliverables