Long-Term Expectations for the Treatment of MGP Residuals by Chemical Oxidants

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API

Introduction

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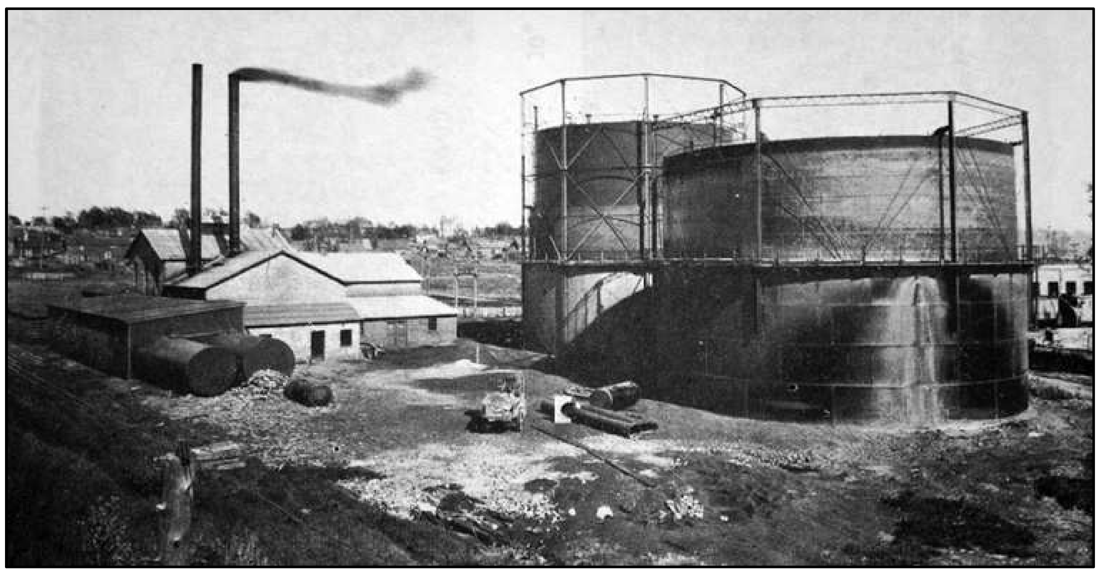
- Before 1950, 1000s of plants manufactured combustible gas for urban use

- Process operations and poor residual management practices



Introduction

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- About 1500 former MGP sites in the United States (USEPA)

- Remediation activities limited to isolation and removal of source material

Introduction

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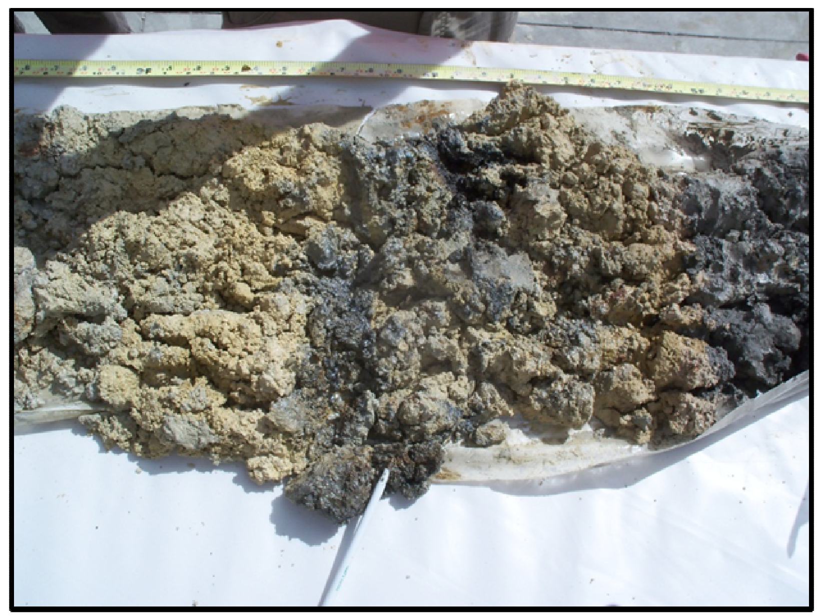
- MGP residuals are multi-component NAPLs
- large number of compounds
- weathering has produced higher MW mixture



Issues

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- ChemOx treatment is promising
- Impacts on MGP residuals are unknown
- Hence long-term behaviour (> 5 years) of dissolved phase concentrations is a concern

Approach

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- Impacted soil and groundwater obtained from a MGP site located in Florida.

- End-point expectations and potential constraints were evaluated by treatability batch experiments.

- Physical model experiments using impacted sediments

- A single cell numerical model was developed.

NAPL Composition

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Organic Compound	Concentration mg/kg	MDL mg/kg	Percent of Identified
BTEX			
Benzene	2640	11.40	0.77
Ethylbenzene	4480	8.09	1.32
m-Xylene & p-Xylene	1880	8.09	0.55
o-Xylene	738	7.83	0.22
Toluene	32.3	10.10	0.01
Trimethylbenzenes			
1,2,3-Trimethylbenzene	734	8.35	0.22
1,2,4-Trimethylbenzene	2260	7.75	0.66
1,3,5-Trimethylbenzene	756	8.61	0.22
Methylethylbenzene			
1-Methyl-2-ethylbenzene	395	6.37	0.12
1-Methyl-3-ethylbenzene	2200	11.8	0.65
1-Methyl-4-ethylbenzene	1660	10.6	0.49
Hydrocarbons			
Dodecane	880	41.7	0.26
Hexadecane	11200	28.8	3.29
Nonacosane	1610	128	0.47
Octadecane	1940	38.4	0.57
Pentacosane	3060	101	0.90
Pentadecane	16400	22.8	4.81
Tetradecane	1740	28.8	0.51
Tridecane	560	52.2	0.16
Undecane	1360	57.2	0.40
PAHs			
1-Methylnaphthalene	25500	1100	7.49
2-Methylnaphthalene	46700	990	13.71
2,6-Dimethylnaphthalene	11500	3.41	3.38
2,3,5-Trimethylnaphthalene	1000	2.35	0.29
Acenaphthene	13300	2.53	3.90
Acenaphthylene	4050	2.74	1.19
Anthracene	6280	2.96	1.84
Benz (a) anthracene	3180	2.93	0.93
Benzo(a)fluoranthene	702	2.85	0.21
Benzo (a) pyrene	3160	4.10	0.93
Benz (b, k) fluoranthene	2890	2.85	0.85
Benzo(b)fluorene	1450	4.16	0.43
Benzo (g,h,i) perylene	1230	3.82	0.36
Benzothiophene	883	4.50	0.26
Biphenyl	4990	4.44	1.46
Carbazole	61	4.70	0.02
Chrysene	2810	2.90	0.82
Dibenzofuran	1500	4.52	0.44
Fluoranthene	7930	4.56	2.33
Indane	11200	92.1	3.29
Indene	1700	4.34	0.50
Fluorene	7720	3.83	2.27
Indeno[1,2,3-c,d] pyrene + Dibenz [a,h] anthracene	1309	3.90	0.38
Naphthalene	83800	625	24.60
Phenanthrene	26400	23.8	7.75
Pyrene	12900	3.78	3.79
Total (identified)	340670		

- **46 compounds**
- **34% identified**
- **66% unidentified (bulk)**

Aqueous Treatability

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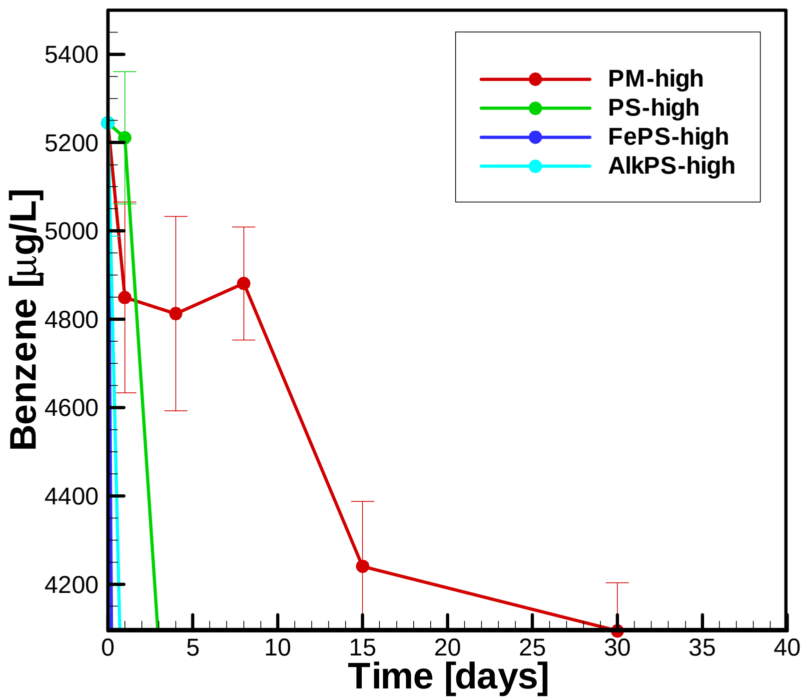

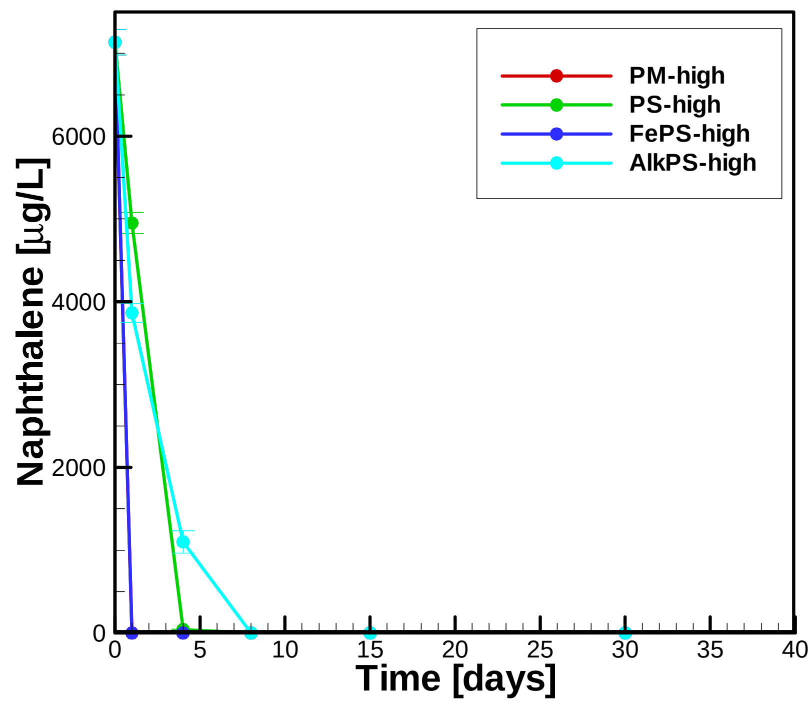

Slurry Treatability

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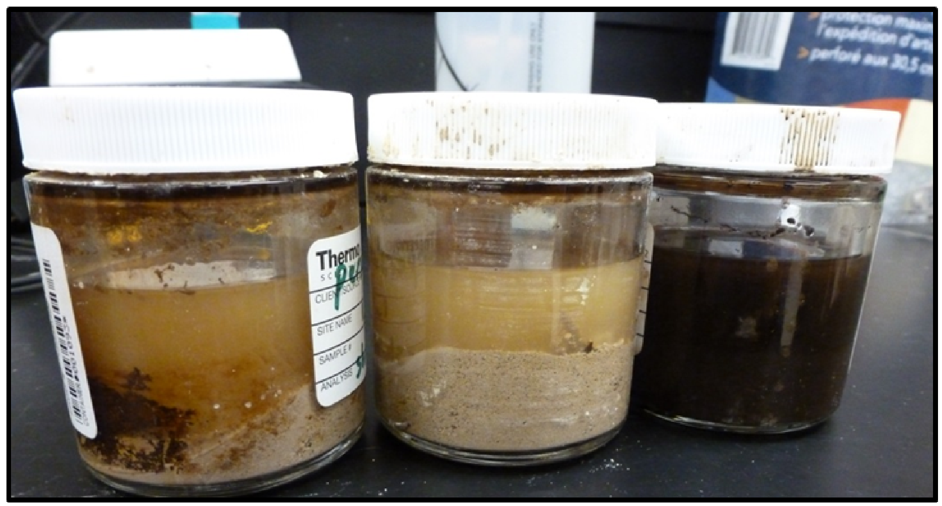
Experimental series:

- permanganate (PM)
- unactivated persulfate (PS)
- alkaline (pH of 11) activated persulfate (AlkPS)



Slurry Treatability

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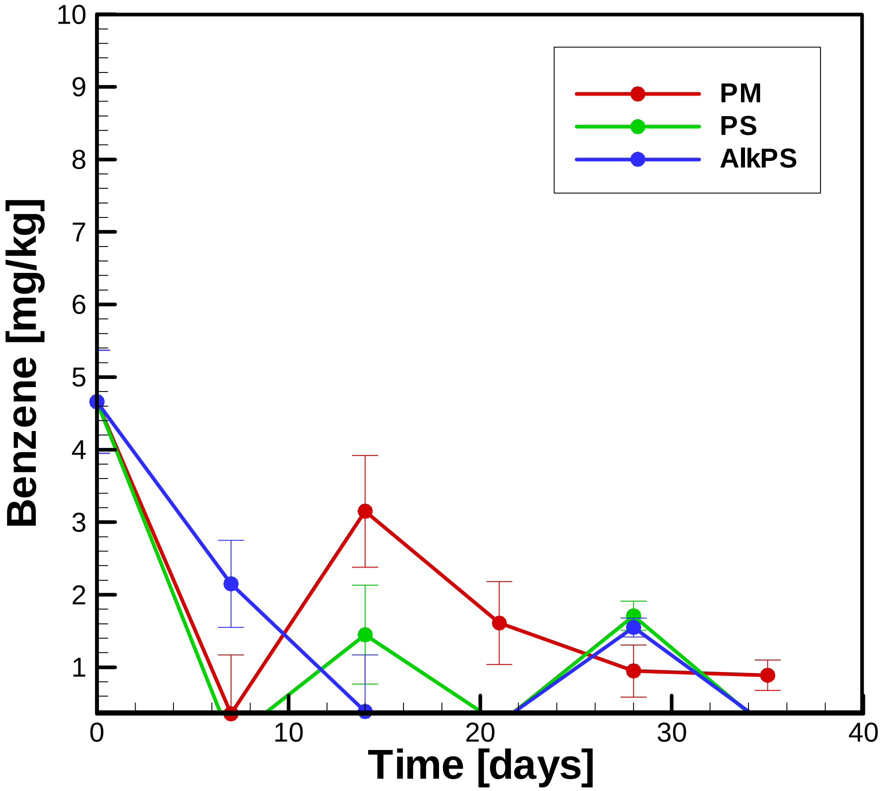

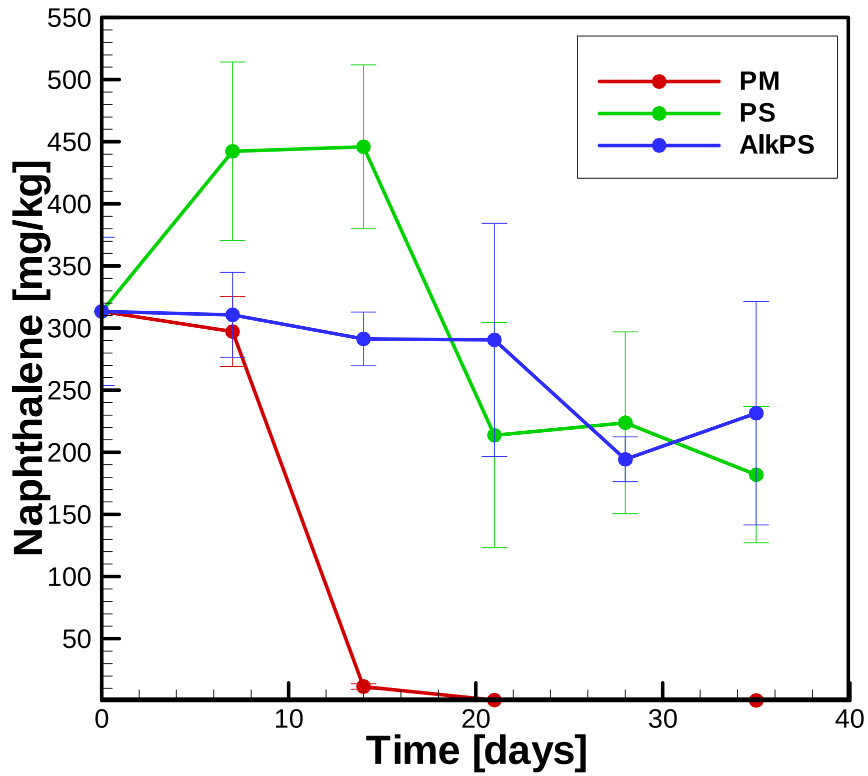

PM>95%	PS>70%	Alk-PS>65%

Physical Model

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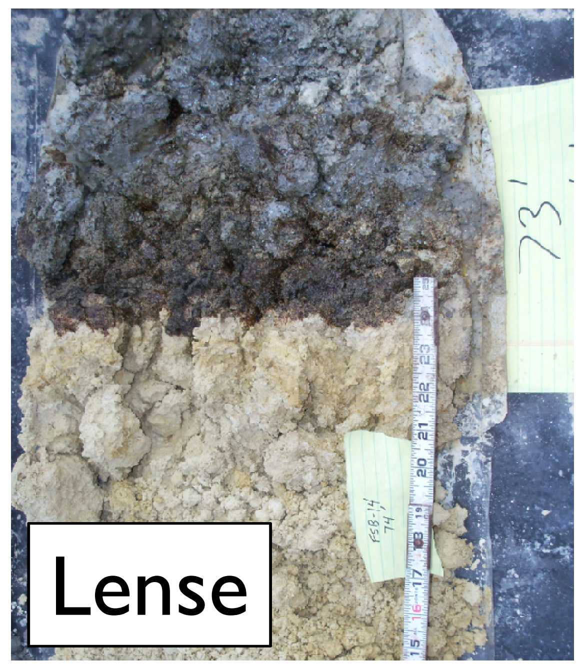
- **explore the temporal expectations for ISCO treatment of the various NAPL architectures observed**



Physical Model

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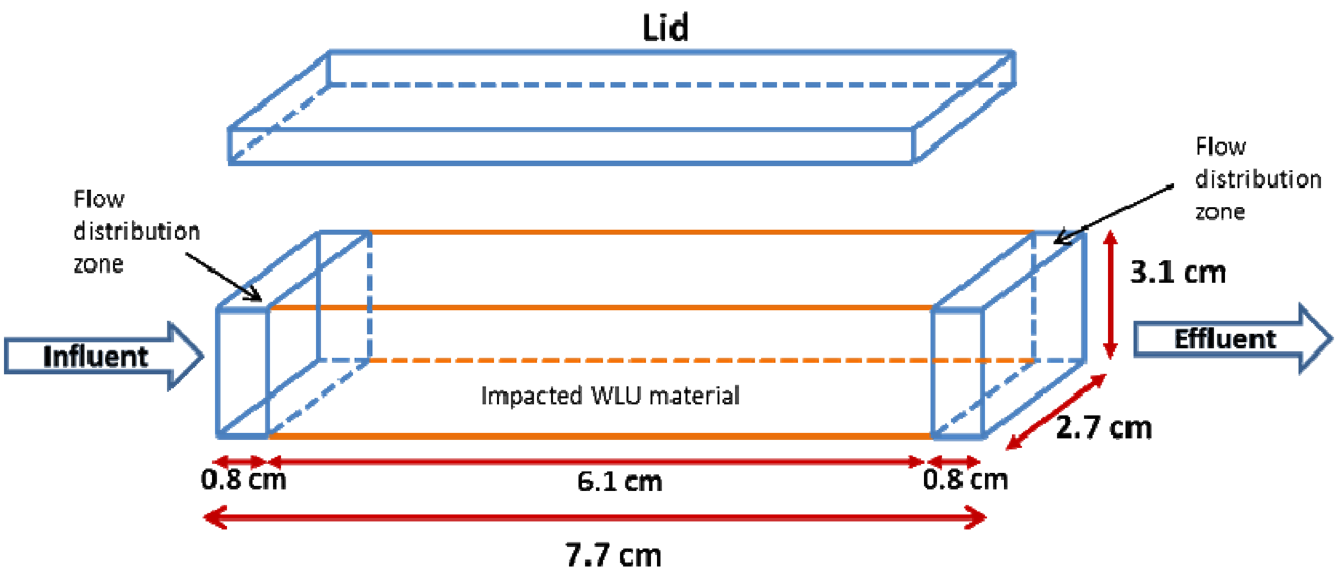

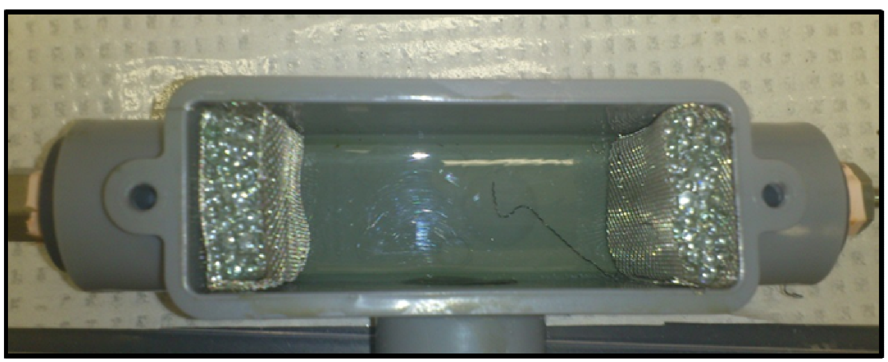

System Operation

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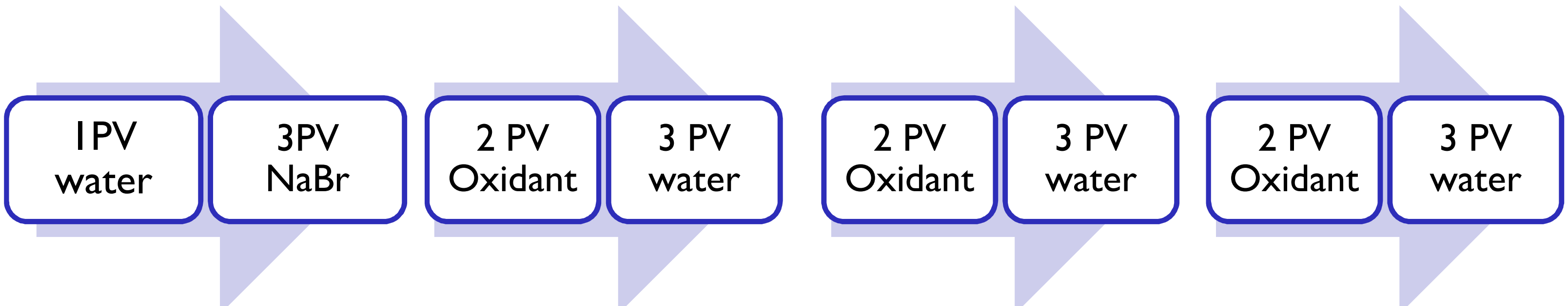
Flushing timeline



Controls - COC

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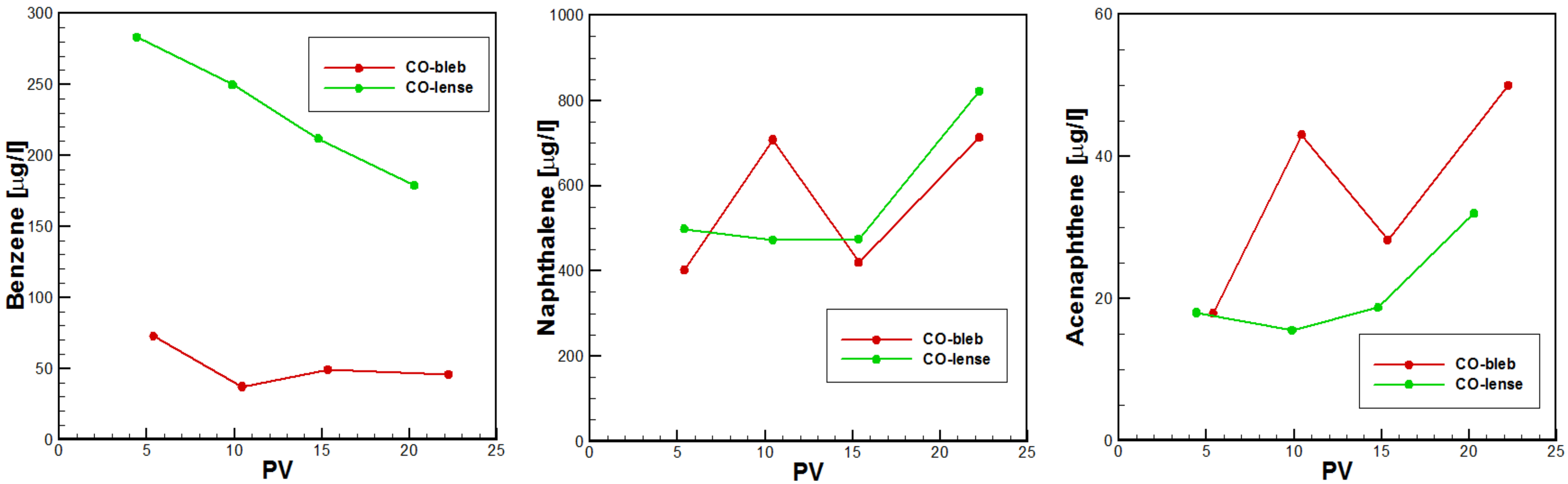

Controls – Soil COCs

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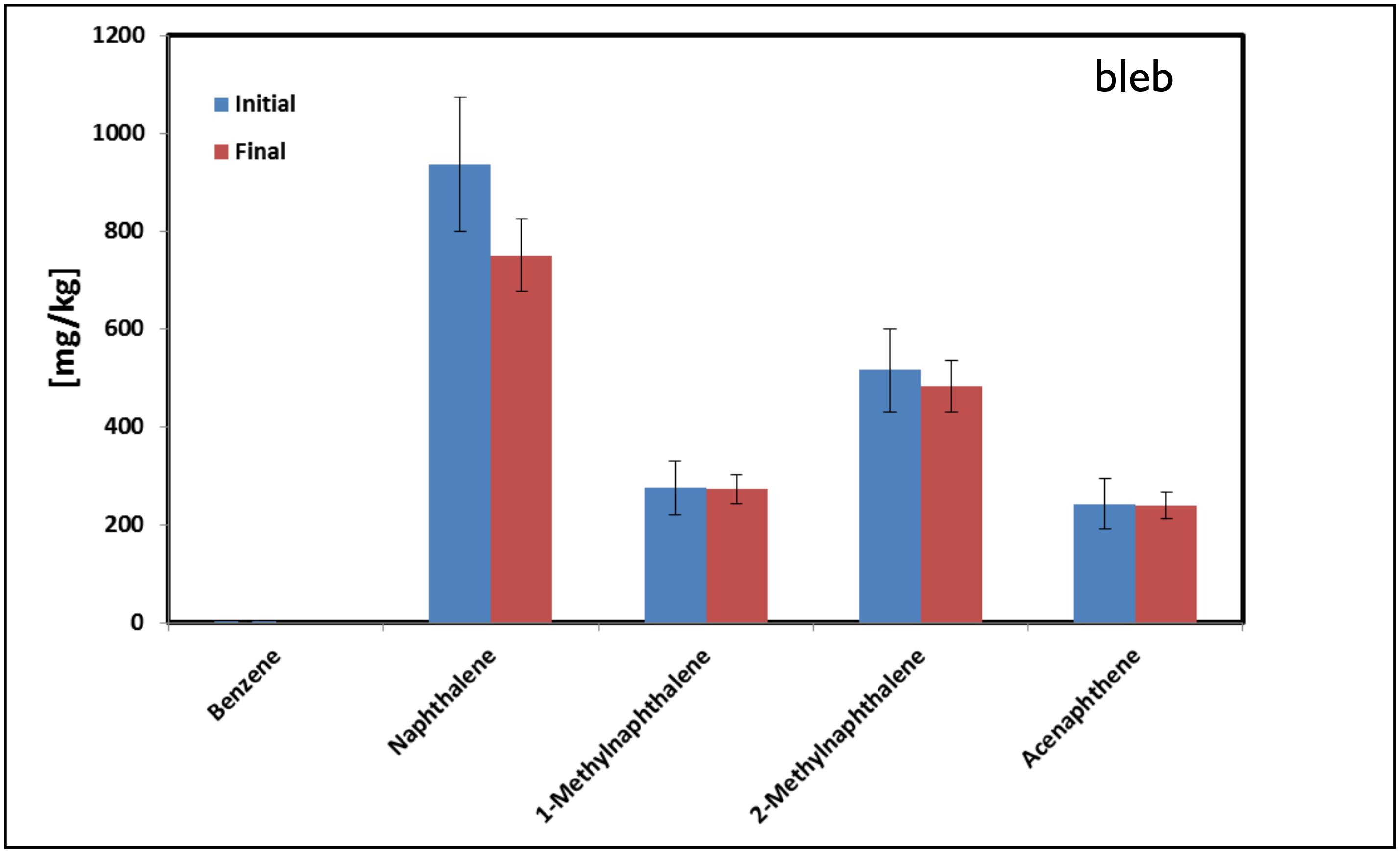

Oxidant Profiles

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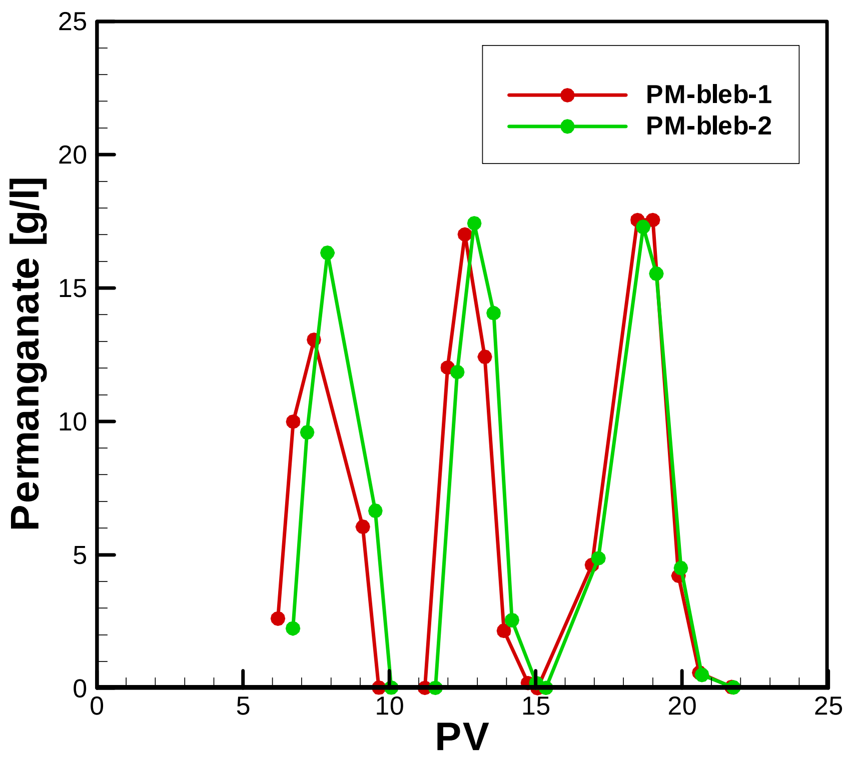
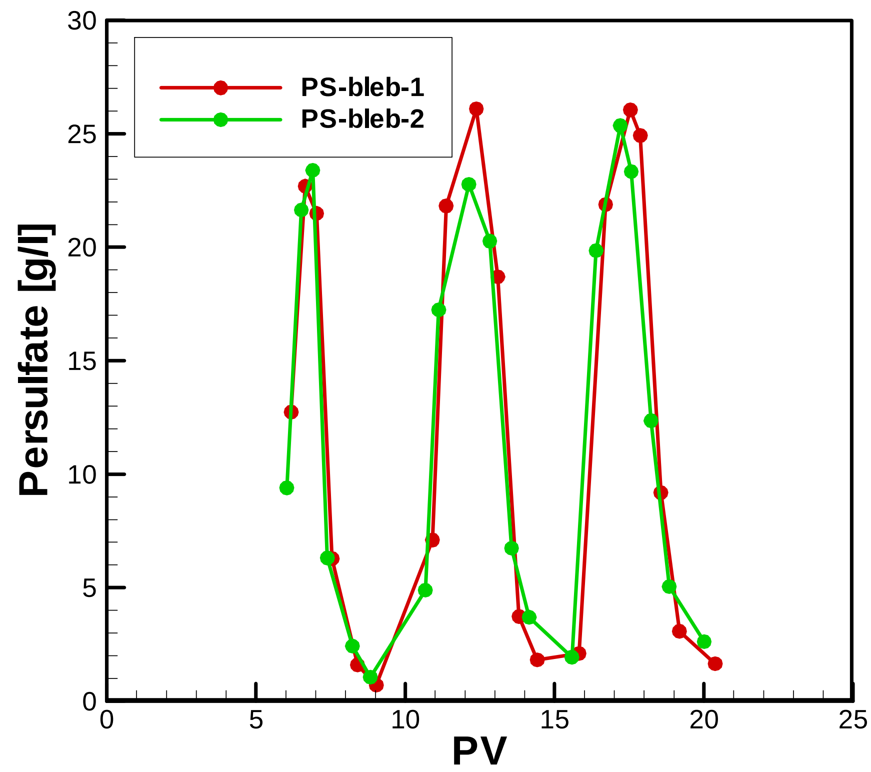
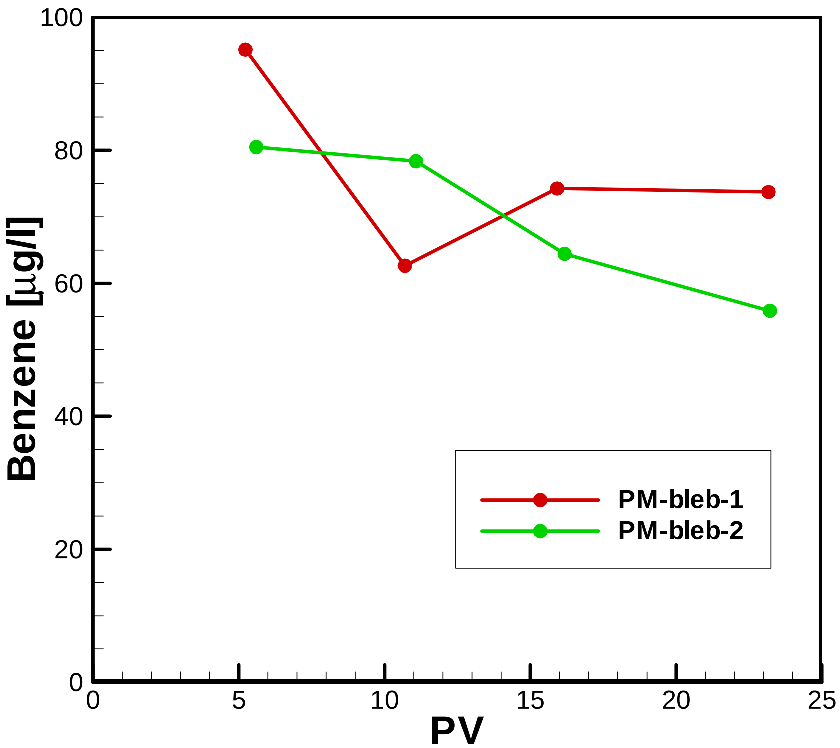
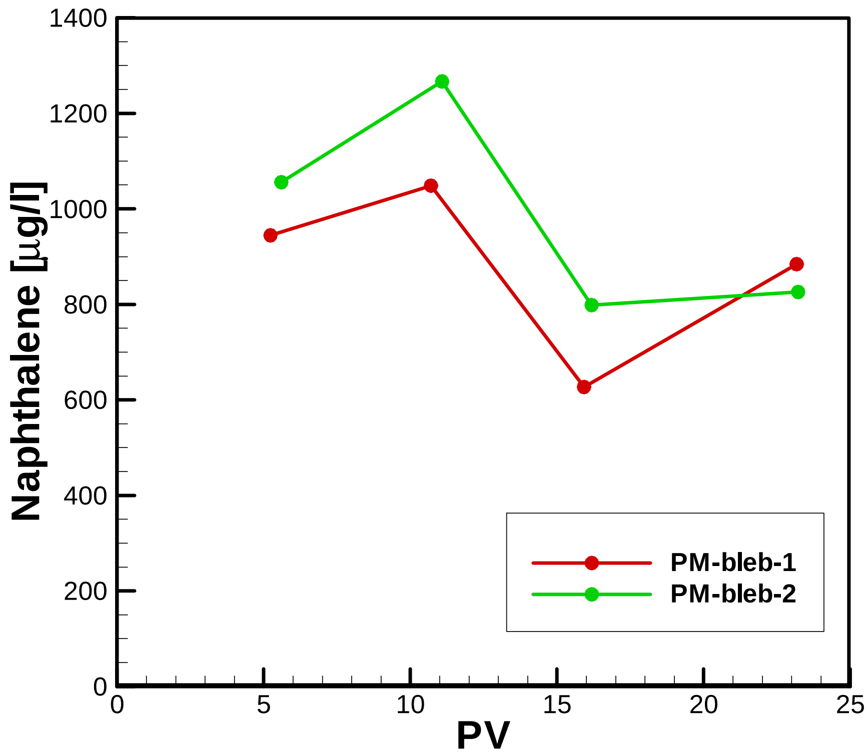


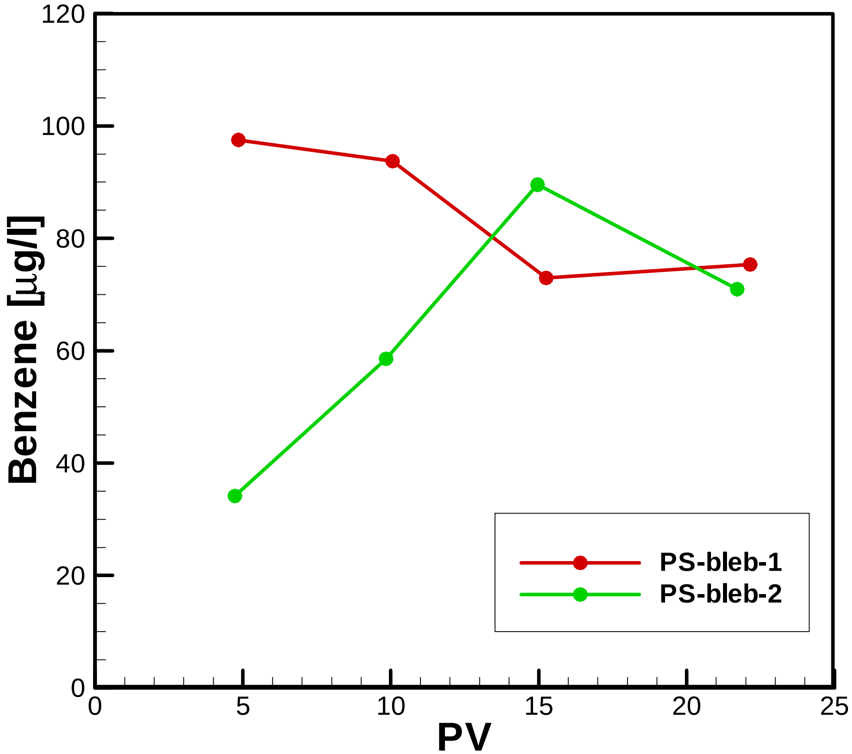


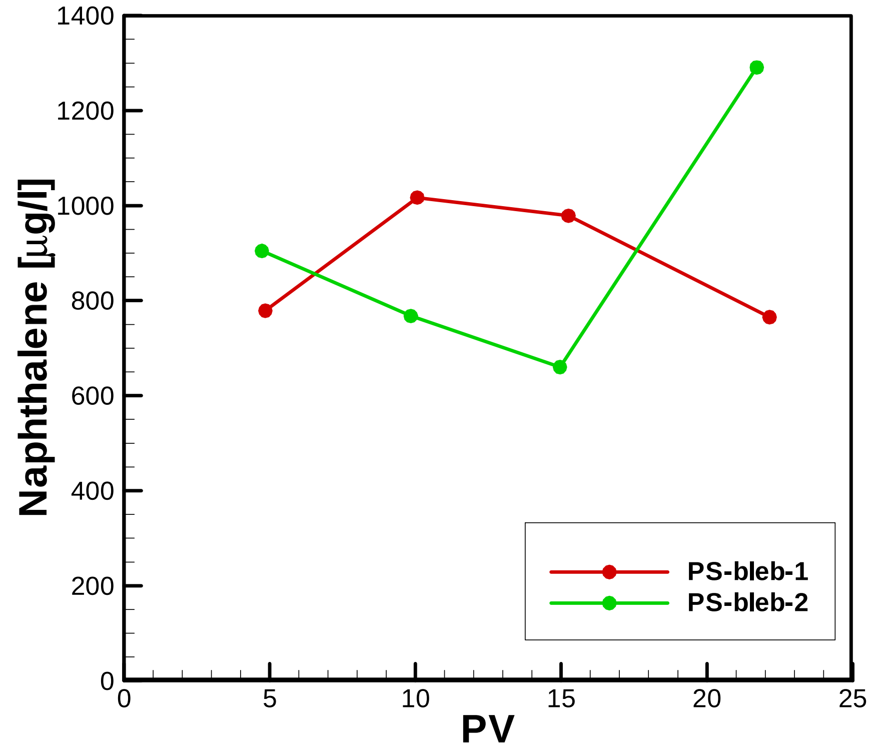
PM - bleb


100
80
60
40
20
0
0
5
10
15
20
25
PV
Benzene [μg/l]
PM-bleb-1
PM-bleb-2


1400
1200
1000
800
600
400
200
0
0
5
10
15
20
25
PV
Naphthalene [μg/l]
PM-bleb-1
PM-bleb-2

PS - bleb


Benzene [μg/l]
PV
PS-bleb-1
PS-bleb-2
0
20
40
60
80
100
120
0
5
10
15
20
25


Naphthalene [μg/l]
PV
PS-bleb-1
PS-bleb-2
0
200
400
600
800
1000
1200
1400
0
5
10
15
20
25

Bleb – Soil COCs

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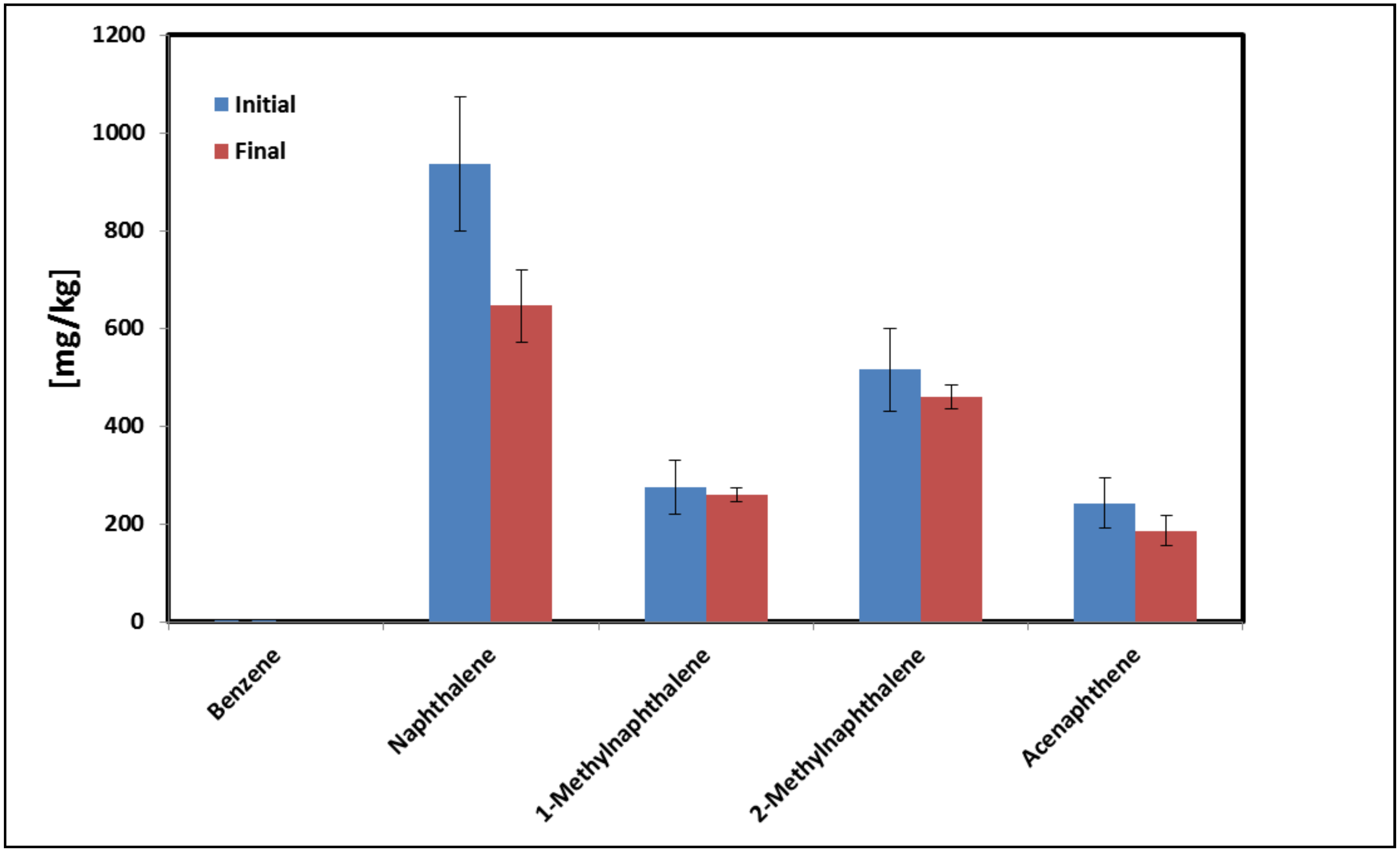
Permanganate



Bleb – Soil COCs

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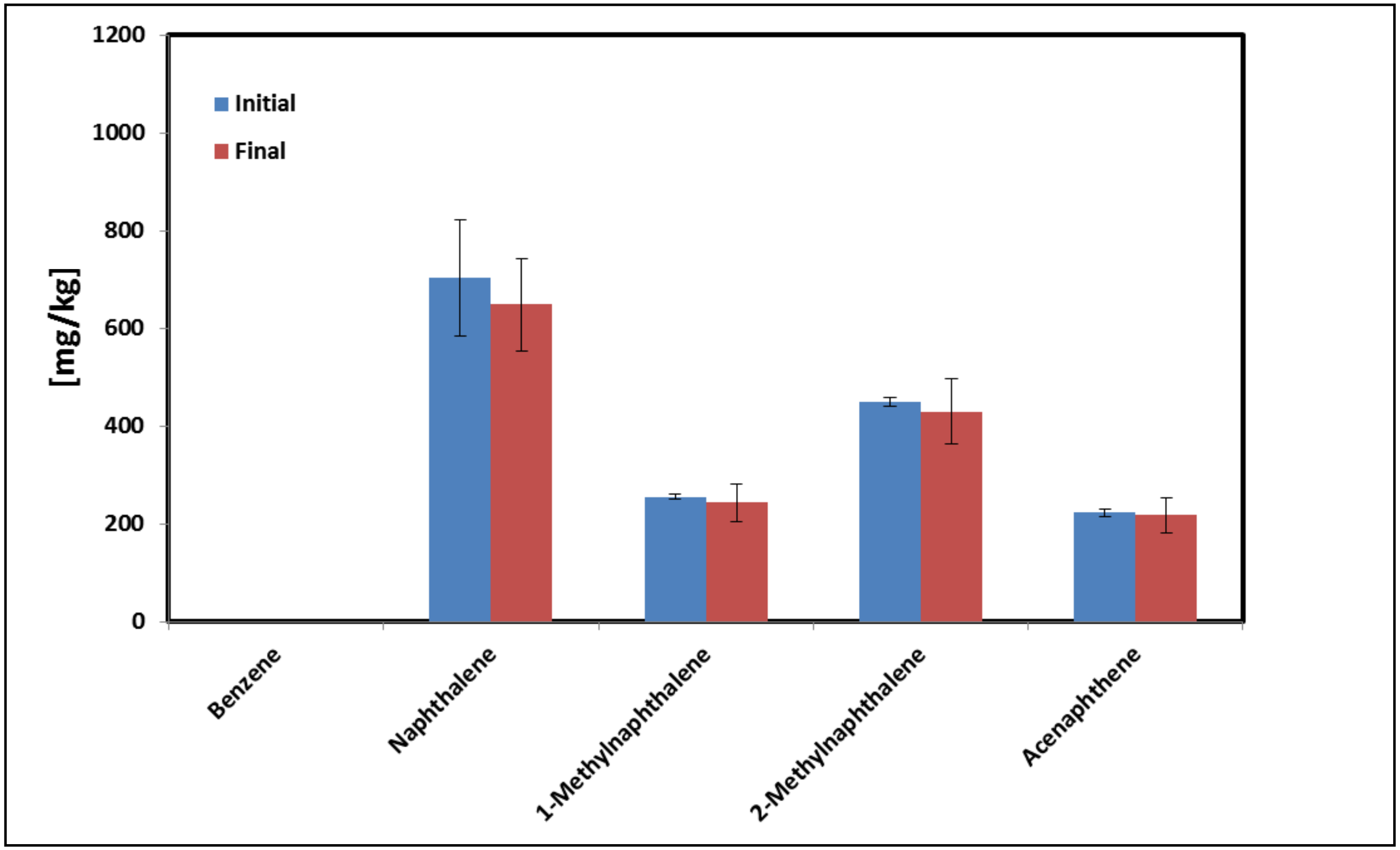
Persulfate



Oxidant mass balance

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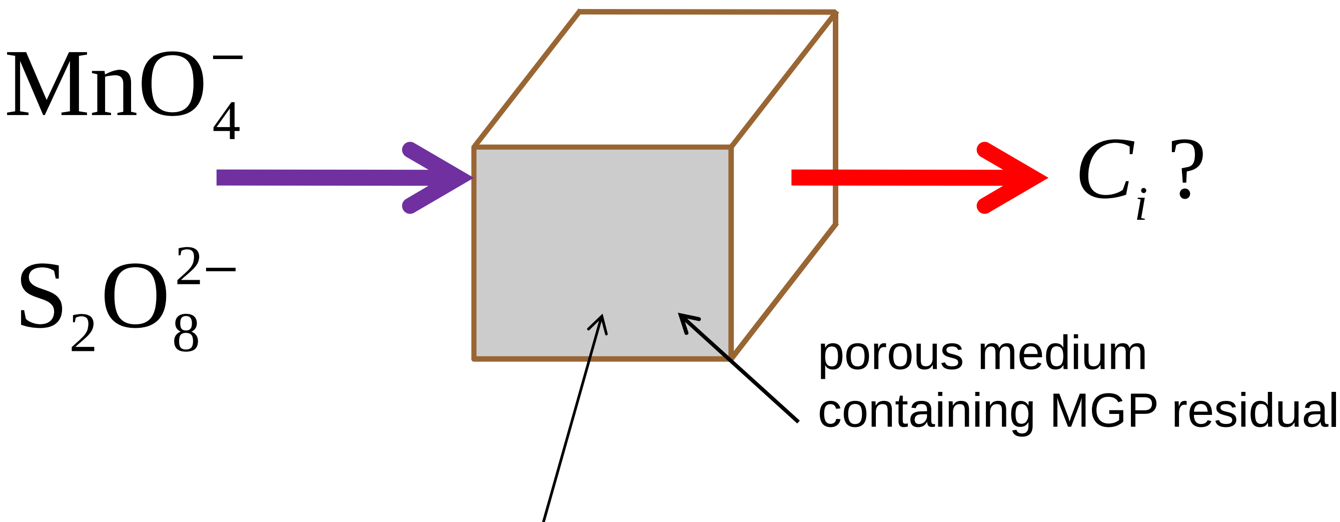
Bleb architecture:

- **50% of the permanganate mass injected was consumed**
- **18% of the persulfate mass injected was consumed**

Treatment Expectations

- **a single cell numerical model was used**



- 22+1 compounds (28% identified)
- Second-order rate oxidation
- Biological degradation
- First order rate mass transfer
- Raoult's law with sub-cooled liquid solubility

Modeling Strategy

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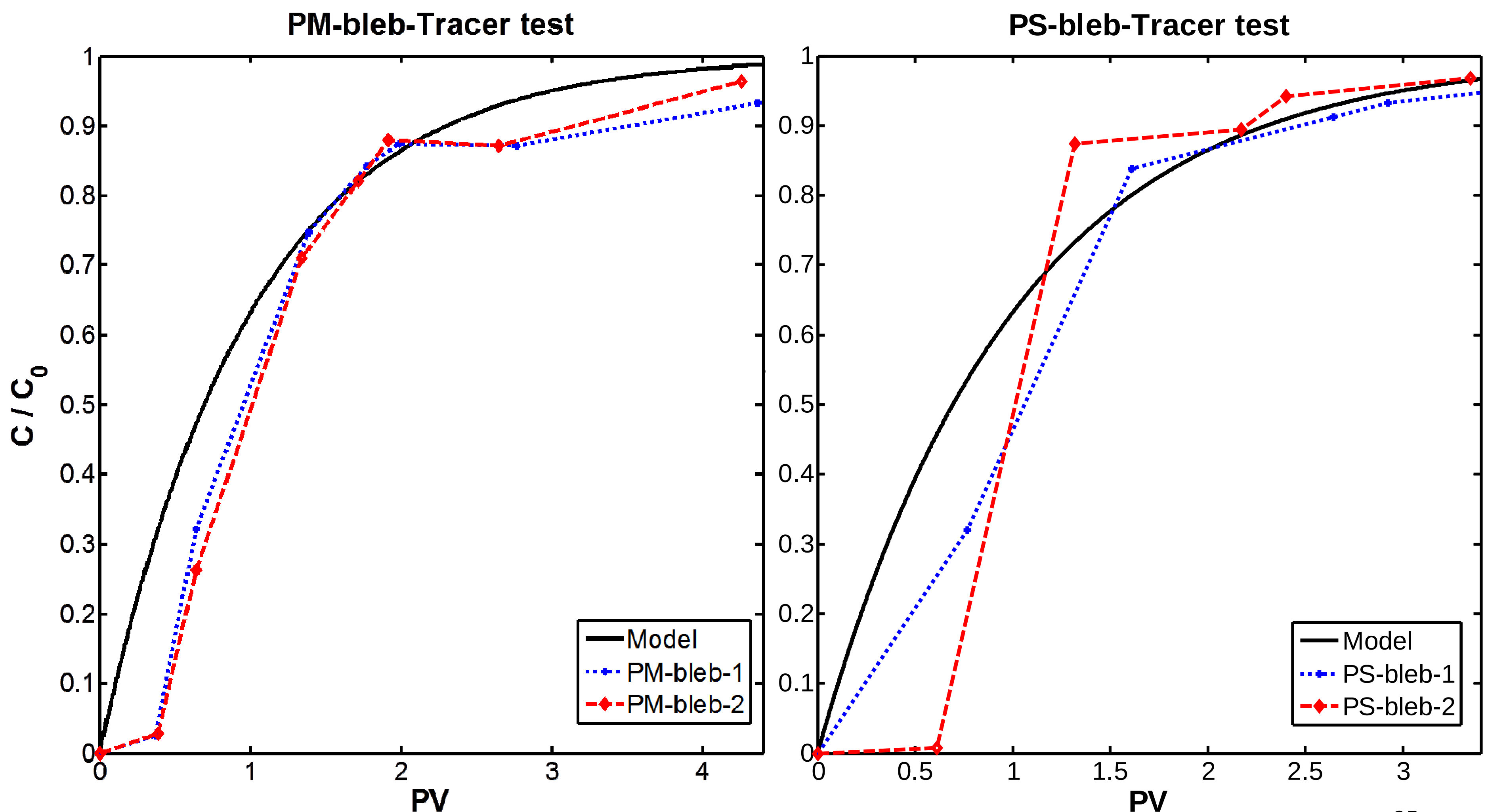
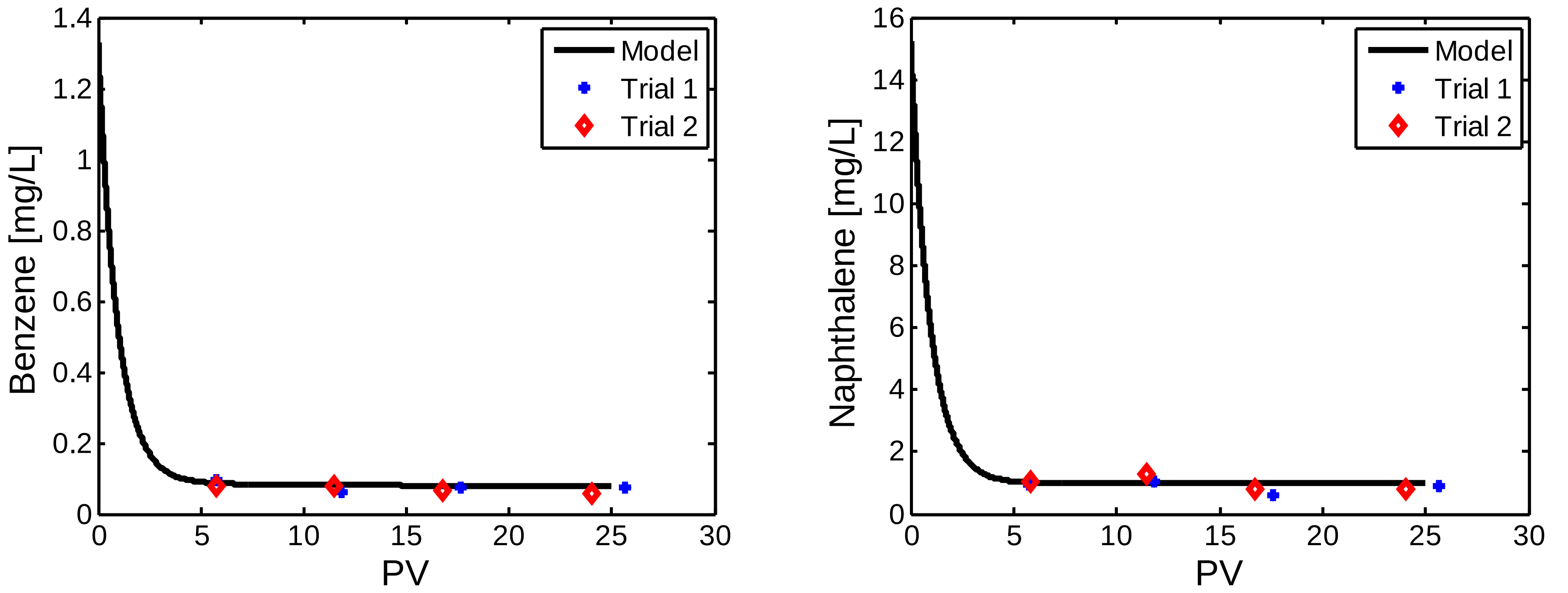
1. **Initial NAPL composition & saturation**
2. **Tracer tests - effective porosity**
3. **Initial effluent concentrations - λ**
4. **Effluent oxidant concentrations**

Tracer Tests



PM-bleb Mass Transfer (λ)



Mass Transfer (λ)

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System	Sn(%)	Porosity	λ (1/day)
PM-bleb	6.4	0.28	0.09
PM-lense	6.6	0.35	0.14
PS-bleb	4.3	0.35	0.06
PS-lense	7.9	0.35	0.10

PM-bleb Oxidant

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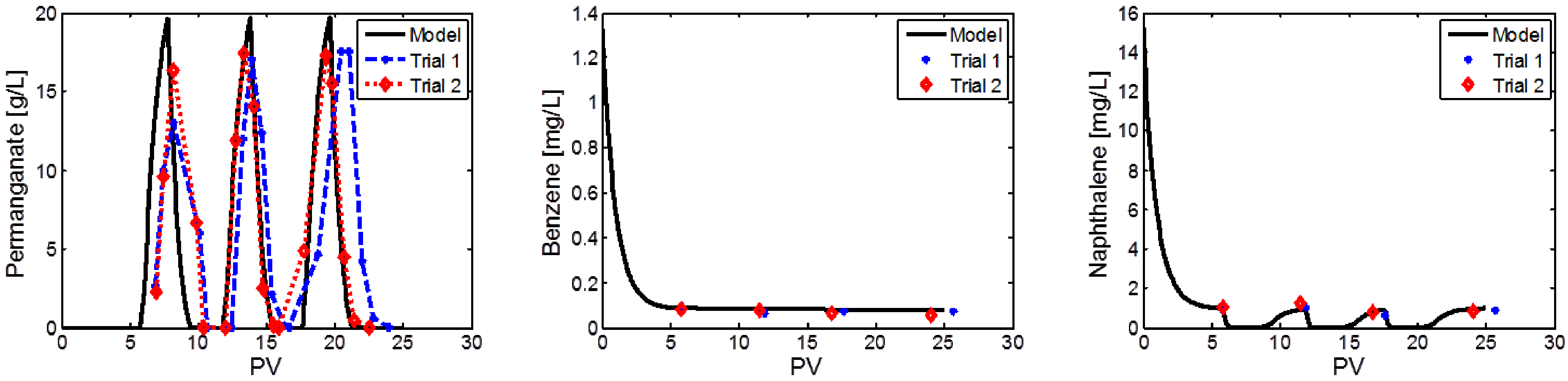

PS-bleb Oxidant

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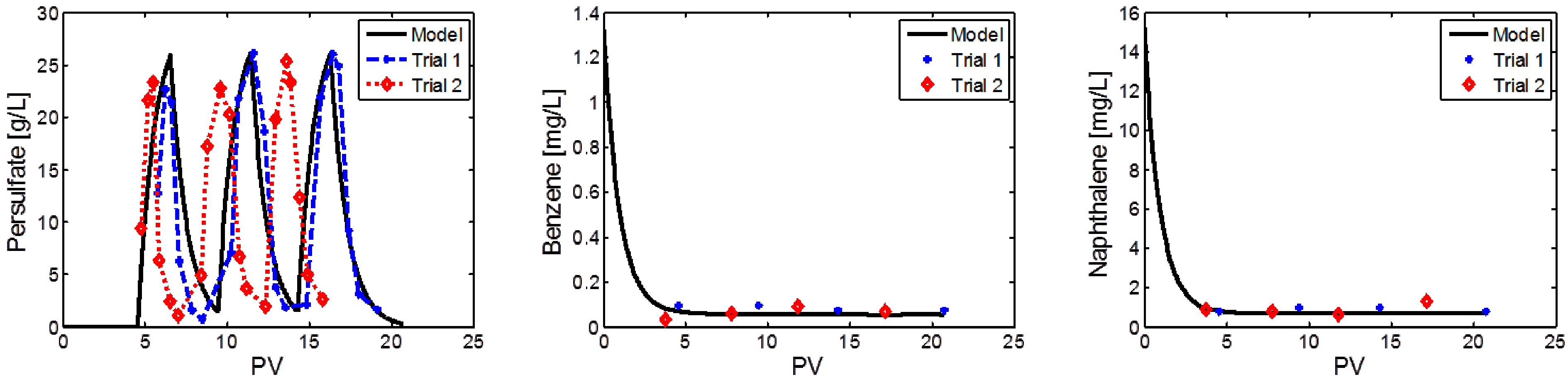

Long-term scenarios

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1. **PM-bleb (baseline)**
2. **PM-bleb (baseline) and no-treatment**
3. **Biological degradation**
4. **Biological degradation + oxidant**

Long-term scenarios

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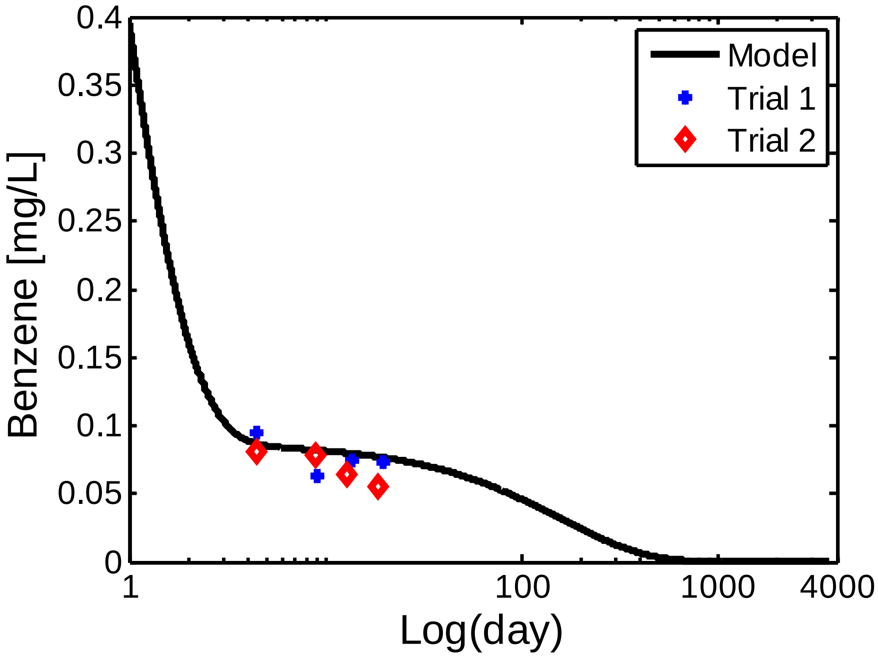
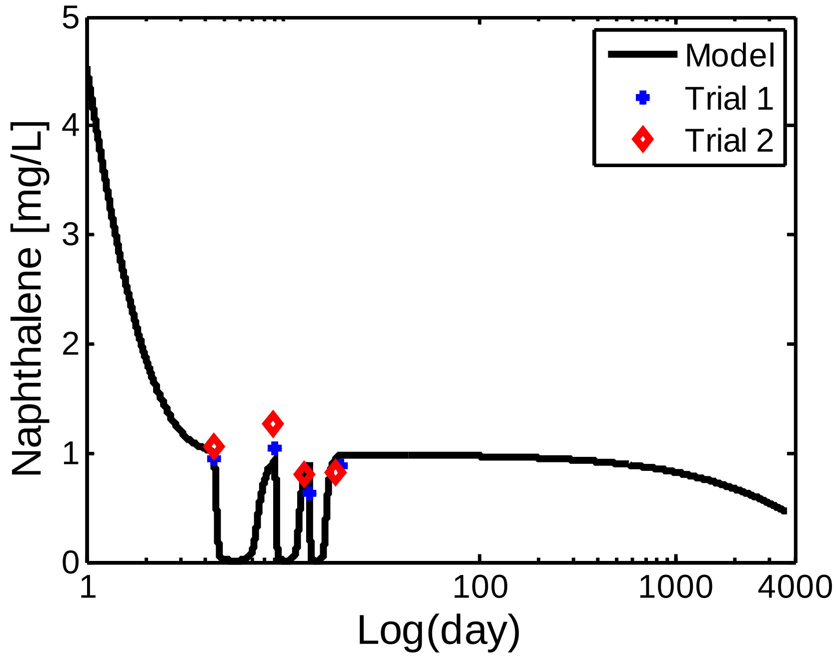
PM-bleb (baseline)

< 1% of non-bulk NAPL mass "oxidized"





Long-term scenarios

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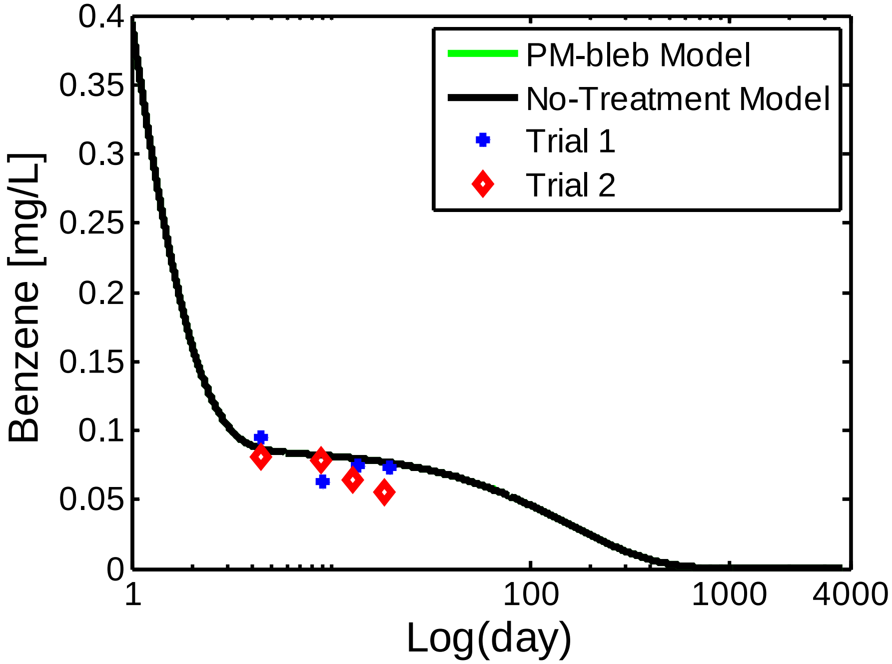
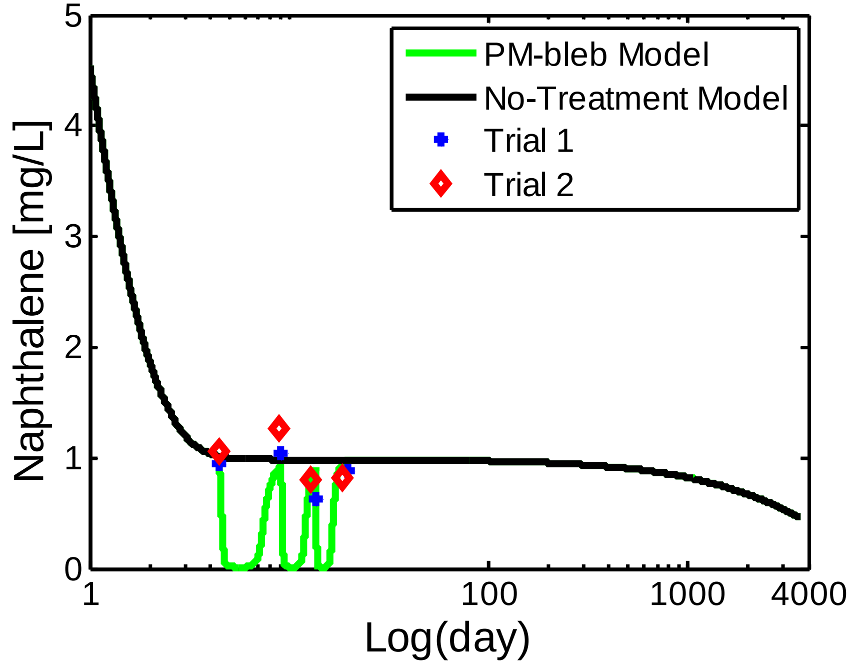
PM-bleb and no-treatment





Long-term scenarios

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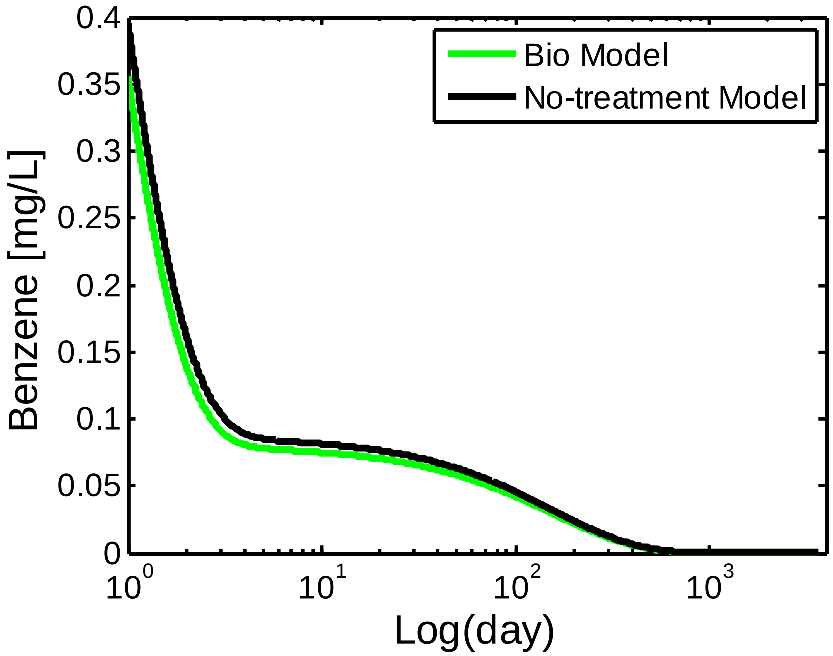
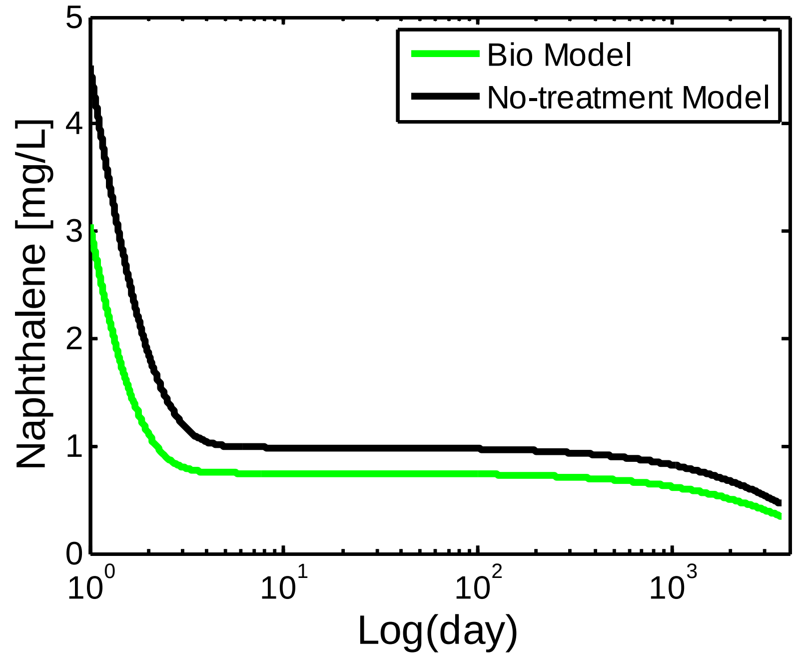
Biological degradation





Long-term scenarios

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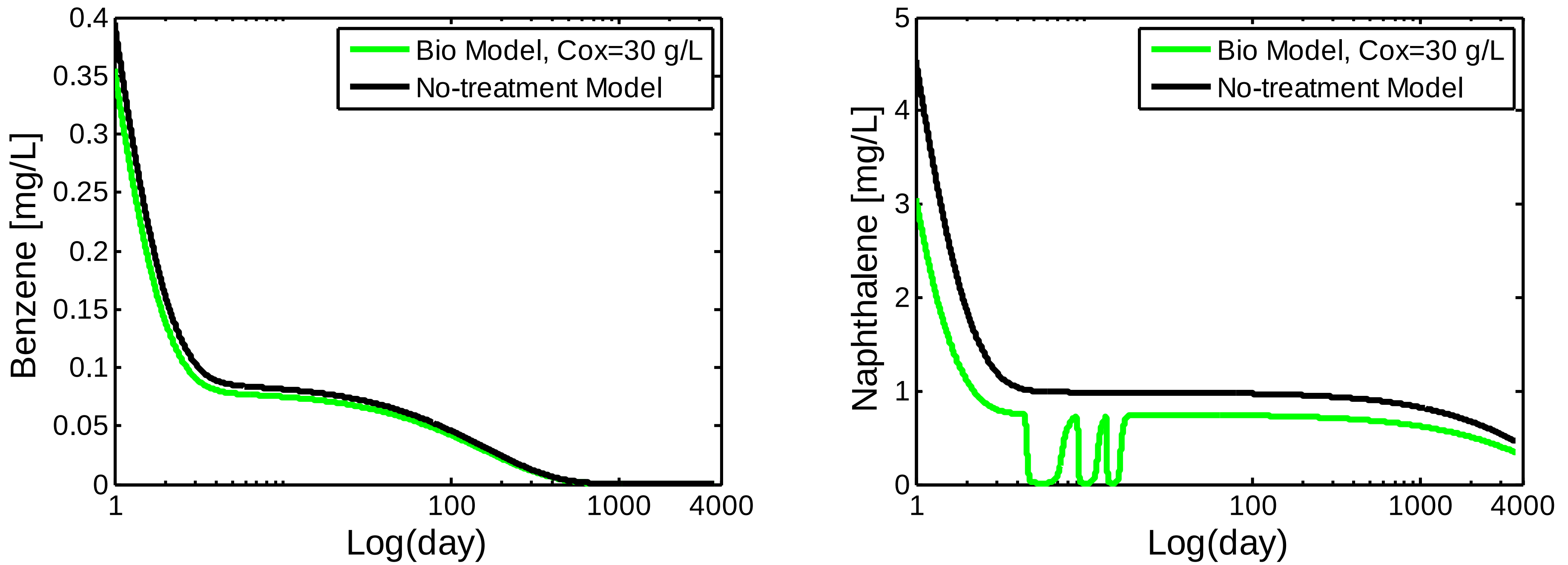
Biological degradation + PM



Sensitivity

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- **Pore velocity (1, 10 and 100 cm/day)**
- **Oxidant concentration (30 vs 100 g/L)**
- **Mass transfer rate coefficient (λ)**

  (0.09, 0.18, 1.8 /day)
- **NAPL saturation (S_n) (0.1, 1, 6.4 %)**

Sensitivity – pore velocity

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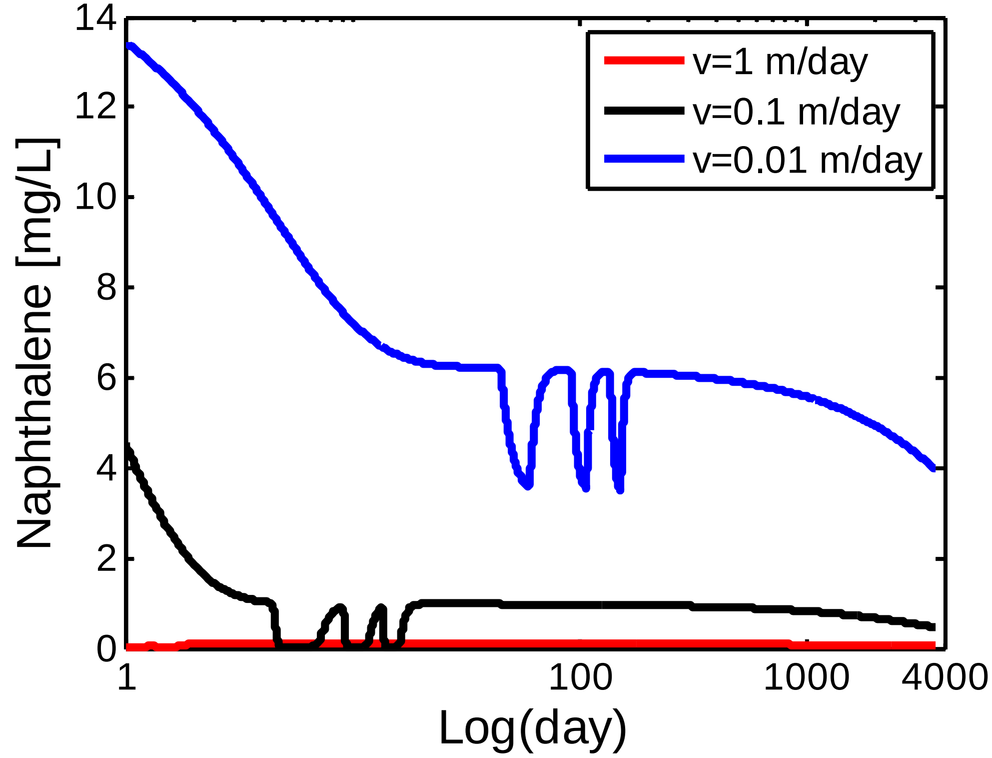

Sensitivity – C_{ox}

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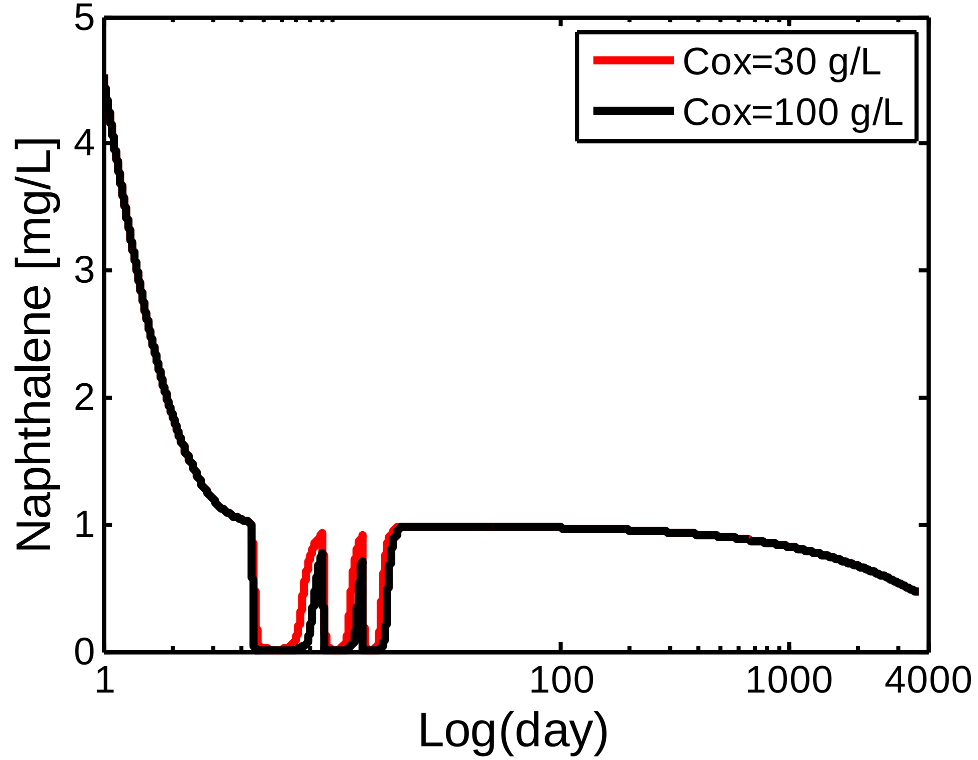

Sensitivity - λ

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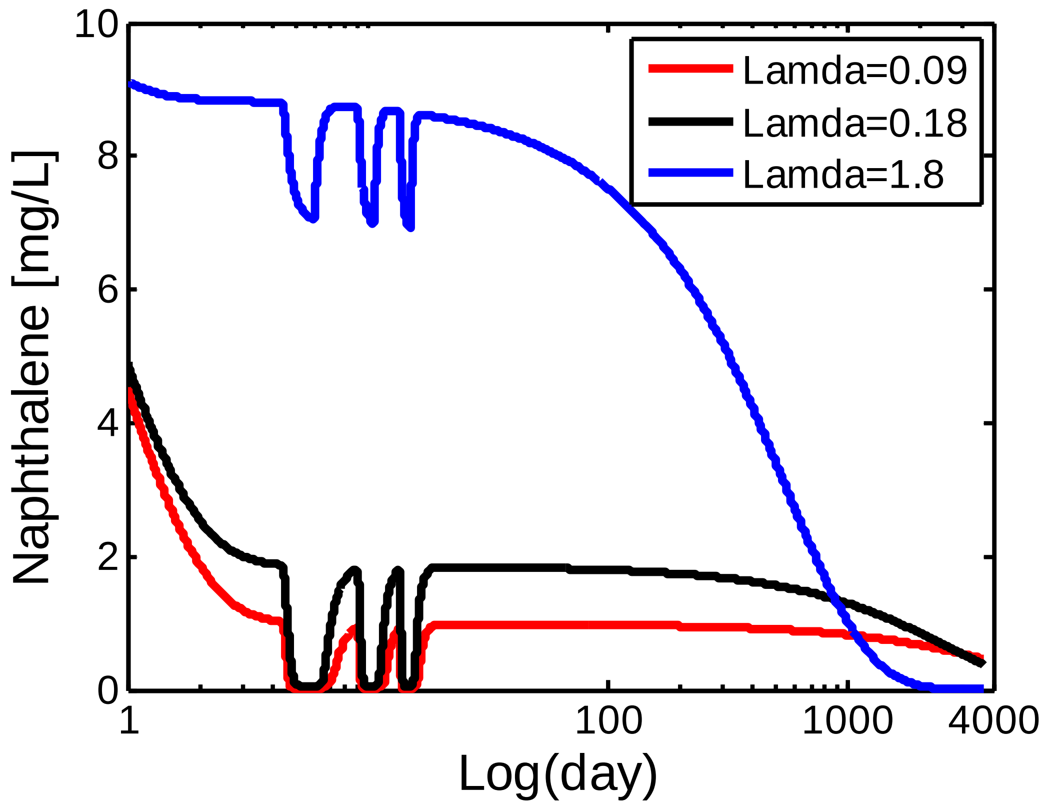

Sensitivity – S_n

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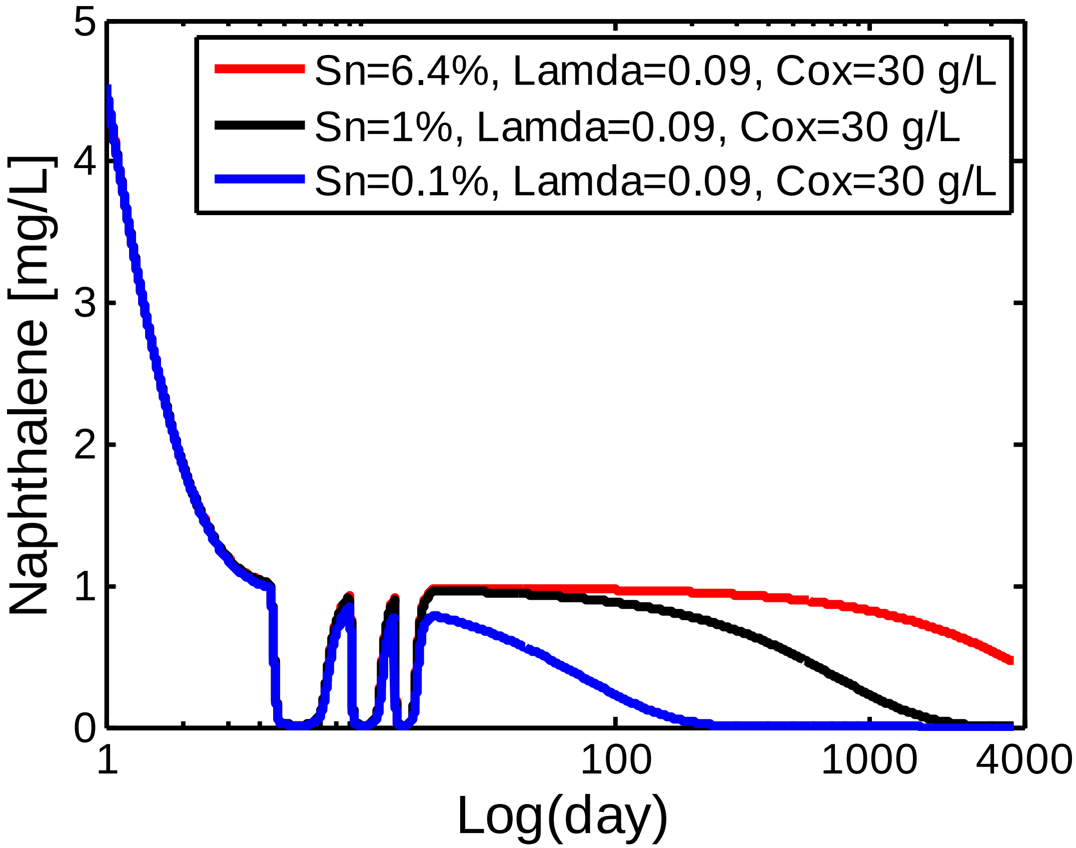

Summary

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- **Degradation of COC mass in aqueous experiments possible**

- **Possible to degrade (65-95%) of "quantified mass" in well-mixed slurry systems**

- **Insignificant "quantifiable mass" lost in all physical model systems**

- **Aggressive treatment with 6 PVs of oxidant results in no change to the long-term plume behaviour relative the "no action" alternative (under model assumptions)**

THANKS