

Hydrophobic Model Systems for Oil Film Photooxidation: Part I: Sensitizer Effects on Hydrocarbon Photodegradation

Supporting information

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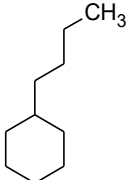
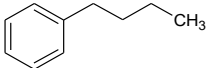
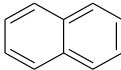
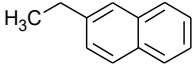
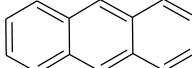
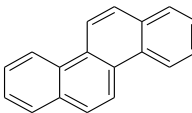
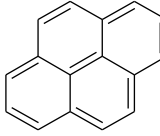
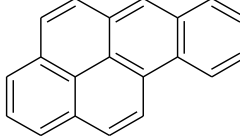
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Table S1: Investigated petroleum hydrocarbons

HCs	Abbr.	GC/MS SIM mass	Typical Conc. in DHW oil (ug/g)*	Chemical structure
Butyl cyclohexane	BCH	83	n.d.	
Butyl Benzene	BBz	91	n.d.	
Naphthalene	NAP	128	855 ug/g 0.66 umol/g	
Ethyl Naphthalene	ENAP	156	n.d.	
Anthracene	ANT	178	3.4 ug/g	
Chrysene	CHR	228	23 ug/g	
Pyrene	PYR	202	15 ug/g	
Benzo[a]pyrene	BaP	252	1.4 ug/g	

* Based on NIST standard reference material 2779

(<https://tsapps.nist.gov/srmext/certificates/2779.pdf>). *n.d.* = not determined.

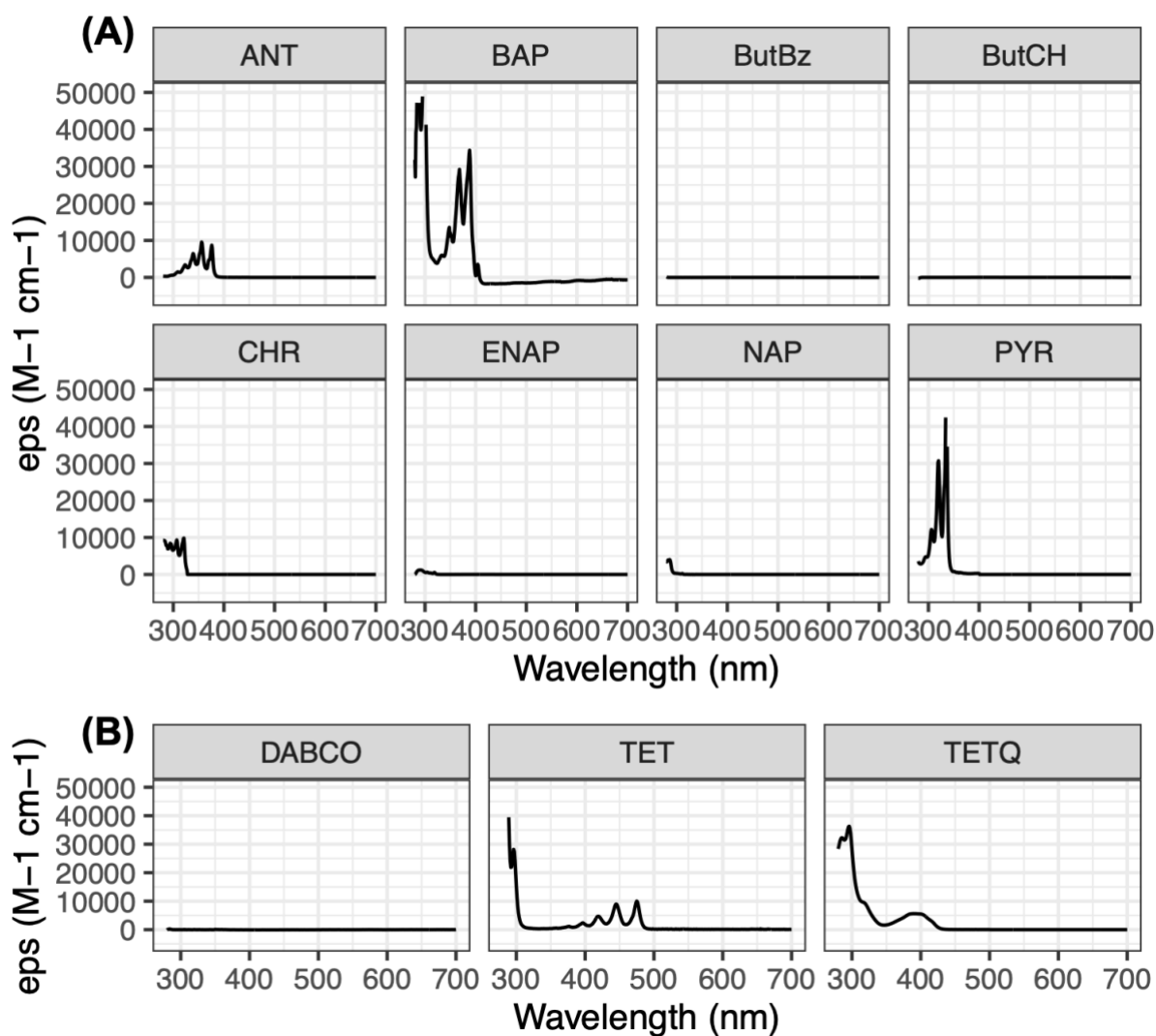


Fig. S1.UV/VIS data: Molar extinction coefficients (epsilon) of (A) target hydrocarbons; (B) sensitizers and scavengers in toluene.

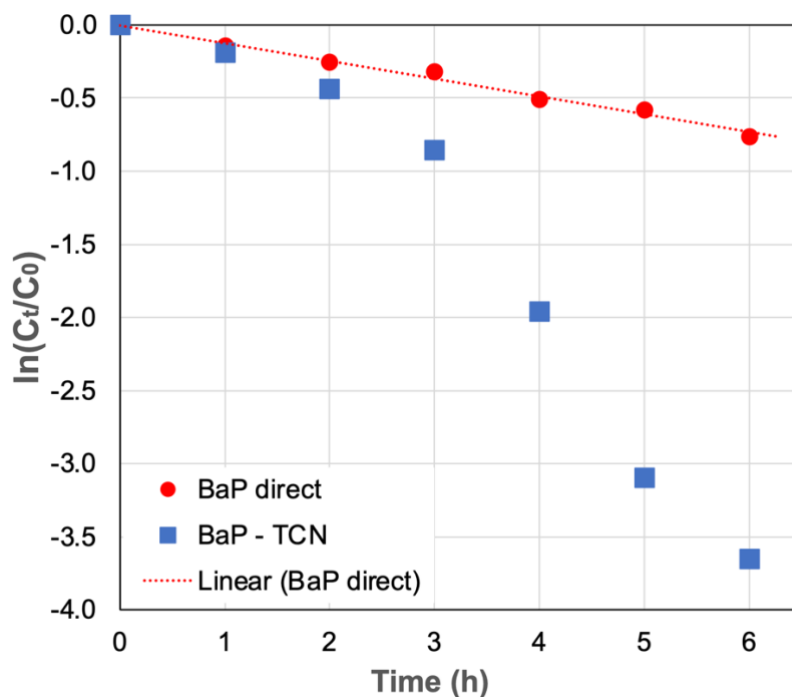


Fig. S2. First-order transformation of BaP degradation data. Direct photolysis of BaP exhibited near-linear behavior ($R^2 = 0.988$), whereas TCN-sensitized degradation deviated substantially from linearity, indicating that a single first-order rate constant does not adequately describe the full irradiation period.

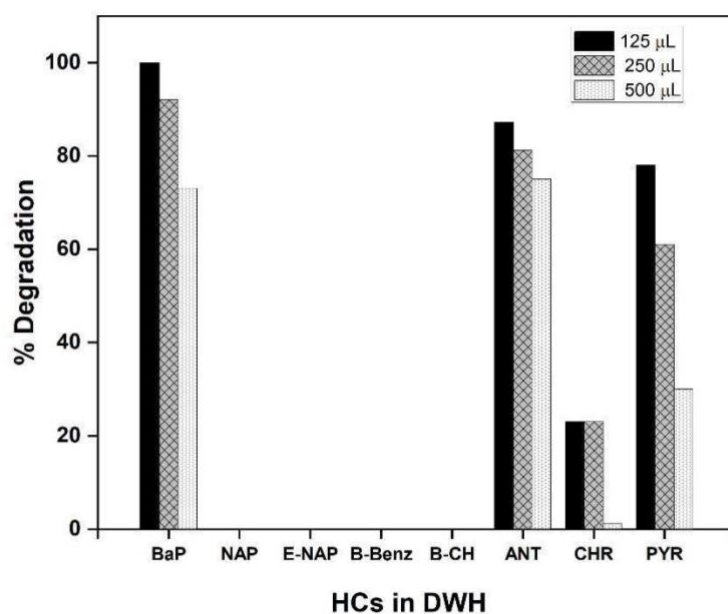


Fig. S3. Effect of DWH content on the photochemical transformation of PAHs; [HCs] = 5 μM, Time 24 hr

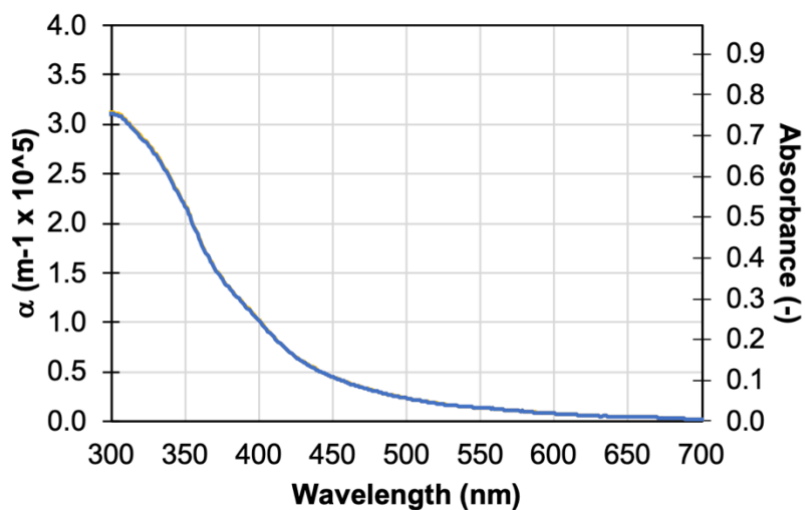


Fig S4. Absorbance of a DWH oil solution in toluene (right axis; concentration = 0.34 mg/mL) and derived neat-oil Napierian attenuation coefficients (α), calculated from absorbance using $\alpha = 2.303 A * \rho / \text{conc.}$ ($\rho = 0431.9 \text{ g/mL}$).

Table S2: Effect of different sensitizers on the degradation of BaP
[sensitizers]₀ = 50 μM

Sensitizer	[BaP] ₀ = 5 μM	
	C _t /C ₀	% degradation
Direct	0.712	28.8
ANT	0.636	36.47
Anthraquinone	0.021	97.64
Tetracene	0.198	80.2
Naphthacene Quinone	0.227	77.3

Table S3: Scavenger effect [BaP] = 5 μM, [TCN] = 100 μM, [Scavenger] = 50 μM;
time 4 hr

Experiments	C _t /C ₀	% degradation
Direct	0.712	28.8
Control (BaP/TCN)	0.198	80.2
No scavenger (BaP/TCN)	0.198	80.2
BaP/TCN/DHP	0.175	82.5
BaP/TCN/Penta diene	0.195	80.5
BaP/TCN/DABCO	0.667	33.3
BaP/TCN/IPA	0.205	79.5

Table S4: Different [BaP] concentration; [TCN] = 100 μM; Time 4 hr

Concentrations of BAP	C _t /C ₀	% Degradation
1 μM	0.08	92.0
5 μM	0.198	80.2
50 μM	0.525	47.5
100 μM	0.706	29.4

Table S5: Effect of TCN on the degradation of BaP; [BaP] = 5 μ M, Time 4 hr

[TCN]	Ct/C0	% Degradation
0 μ M (Direct)	0.691	28.78
5 μ M	0.529	45.45
10 μ M	0.411	57.57
50 μ M	0.265	72.72
100 μ M	0.198	80.2
150 μ M	0.227	77.3

Table S6: Kinetics data; [BaP] = 5 μ M, [TCN] = 100 μ M, [TCQ] = 50 μ M

	TCN	TCQ
	Ct/C0	Ct/C0
0 hr	1	1
1 hr	0.828	0.835
2 hr	0.644	0.506
3 hr	0.425	0.380
4 hr	0.241	0.184
5 hr	0.045	0.084
6 hr	0.026	0.046

Table S7: Estimation of TCN decay and TCQ formation using GC-MS

Tetracene and Quinone formation	Tetracene (peak area)	Concentration of TCN calculated from peak area	Tetracene quinone (peak area)	Concentration of TCQ calculated from peak area
C0 = 50 μ M	6629198		3847789	
1	259960	1.96	2856414	37.1
2	138274	1.04	3137288	40.8
3	98537	0.743	2879916	37.4
4	77436	0.584	2528366	32.9
5	79461	0.599	311738	4.05
6	69940	0.528	268348	3.49

Table S8: Kinetics of BaP direct photolysis; [BaP]= 5 μ M

Time	Ct/C0
0	1
1	0.864
2	0.773
3	0.727
4	0.602
5	0.559
6	0.466

Table S9: Degradation of HCs [HCs] = 5 μ M, [TCN] = 100 μ M, Time 4 hr

HCs	Indirect	Direct
BaP	75.0	38.0
NAP	0	0
Ethyl-NAP	0	0
Butyl Benzene	0	0
Butyl cyclohexane	0	0
Anthracene	27.0	6.0
Chrysene	16.0	4.0
Pyrene	52.0	15.0

Table S10: Degradation kinetics (Ct/C0) of HCs in their mix;
[HCs] = 5 μ M, [TCN] = 100 μ M

	ANT	BaP	BCH	BB	CHR	ENA	NAP	PYR
MIX 5 μ M 0 hr	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
MIX 5 μ M 1 hr	1.19	1.11	1.03	1.07	1.25	1.11	1.01	0.94
MIX 5 μ M 2 hr	1.13	0.80	0.96	1.02	1.19	1.13	1.00	0.87
MIX 5 μ M 3 hr	1.00	0.53	0.90	0.98	1.17	1.14	0.98	0.80
MIX 5 μ M 4 hr	0.78	0.19	1.00	1.06	1.11	1.17	1.05	0.63
MIX 5 μ M 5 hr	0.52	0.06	0.78	0.83	0.87	0.93	0.85	0.35
MIX 5 μ M 6 hr	0.47	0.02	0.65	0.76	0.81	0.94	0.81	0.23

Table S11: Degradation kinetics (Ct/C0) of HCs in dilute DWH crude oil dissolved in toluene; [HCs] = 5 µM, [DWH] = 370 mg crude oil per L toluene.

	ANT	BaP	BBz	BCH	CHR	ENAP	PYR	NAP
Mix DWH 0h	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
DWH 4h	1.00	0.96	0.96	0.90	0.96	1.00	0.96	0.96
DWH 8h	0.40	0.30	1.13	1.15	0.90	1.08	0.64	1.06
DWH 12h	0.33	0.20	0.98	0.95	0.87	1.03	0.58	0.97
DWH 16h	0.13	0.03	0.95	0.88	0.67	1.03	0.22	0.98
DWH 24h	0.11	0.02	0.88	0.85	0.40	0.97	0.09	0.89
DWH 48h	0.10	0.01	1.14	1.29	0.32	0.99	0.04	1.02

Table S12: Scavenging study of HCs in dilute DWH crude oil with added scavengers. [HCs] = 5 µM, [DWH] = 370 mg crude oil per L toluene. [Scavengers] = 50 µM.

	ANT	BaP	BBz	BCH	CHR	ENAP	PYR	NAP
DWH Mix 24 hr	87.27	97.53	-3.08	-11.95	36.58	3.60	81.02	3.05
DWH Mix IPA 24 hr	85.03	97.72	3.07	3.98	30.40	-4.13	77.19	2.77
DWH Mix DABCO 24 hr	78.28	75.09	2.54	-4.25	13.07	0.06	46.18	0.71
DWH Mix Penta diene 24 hr	83.61	96.07	3.90	3.26	28.99	4.91	73.21	9.12