Atmospheric ozone oxidation and photochemical weathering of oil hydrocarbons

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Part I. Atmospheric ozone oxidation of polycyclic aromatic hydrocarbons and dispersed oil in seawater and effects of oil dispersants

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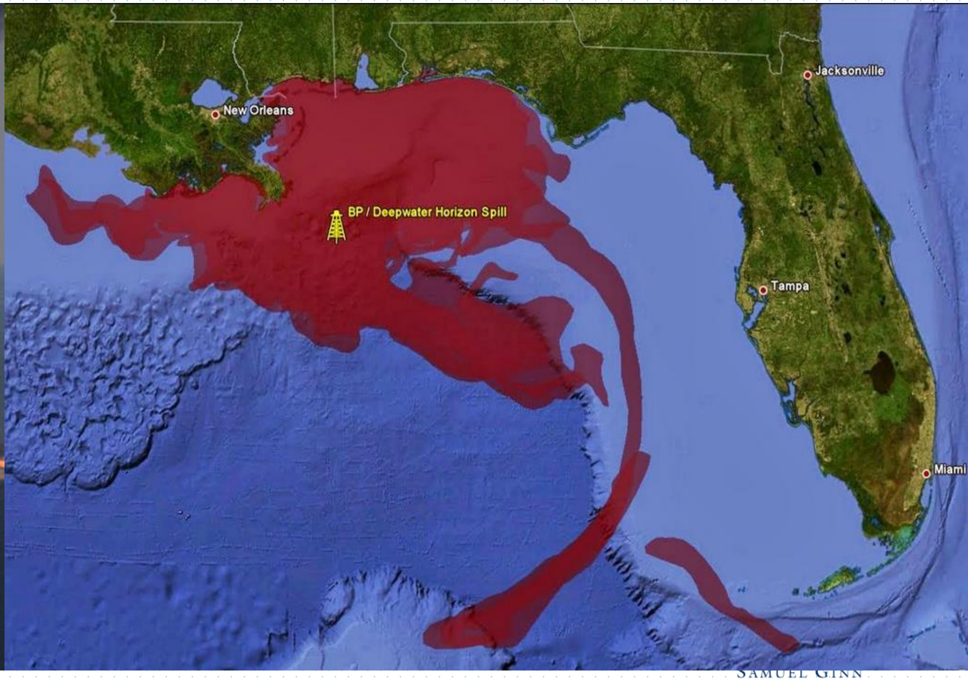
Gong et al. *Chemosphere 2017, 468-475*

The 2010 Deepwater Horizon Oil Spill

- The largest accidental marine oil spill in the history
- About 780,000 m^3 of South Louisiana Sweet Crude oil is released from the BP Macondo well in 87 days



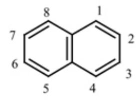
Oil Dispersants

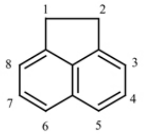
- **BP applied about 7570 m^3 of oil dispersants, including Corexit EC9500A and Corexit EC9527A.**
- **About 16% of the spilled oil was dispersed**

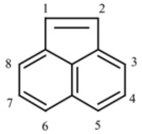
Picture from US Air Force public affairs

PAHs from the DwH oil spill

- **The Macondo oil contained ~3.9% PAHs (2 to 6 rings), i.e., ~21,000 tons of PAHs were released**
- **USEPA listed 16 priority PAHs**


Naphthalene


Acenaphthene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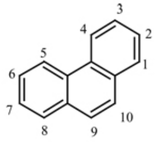
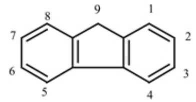
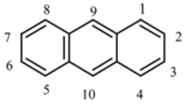
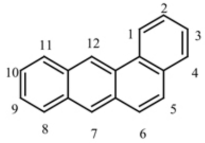
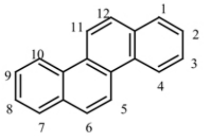
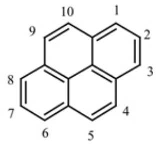

Phenanthrene

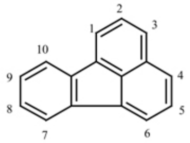

Fluorene

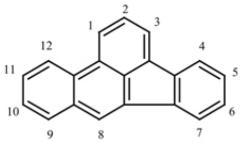

Anthracene

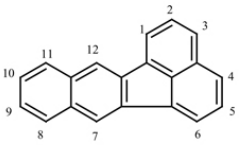

Benz[*a*]anthracene

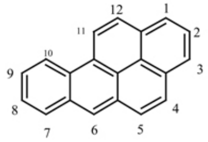

Chrysene

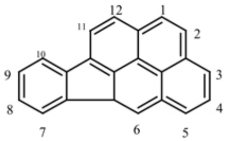

Pyrene

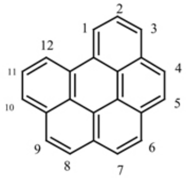

Fluoranthene

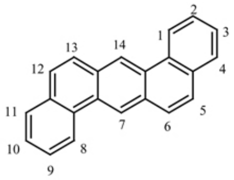

Benzo[*b*]fluoranthene


Benzo[*k*]fluoranthene


Benzo[*a*]pyrene

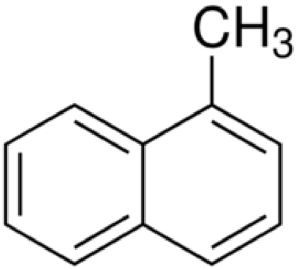

Indeno[1,2,3-*cd*]pyrene

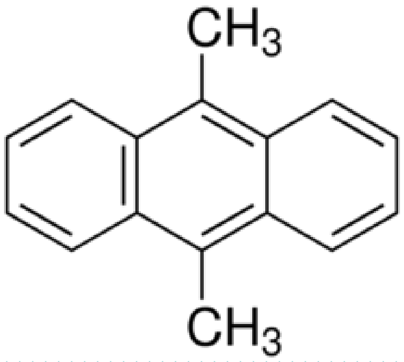

Benzo[*ghi*]perylene

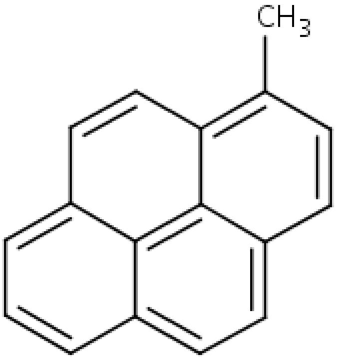

Dibenz[*a,h*]anthracene

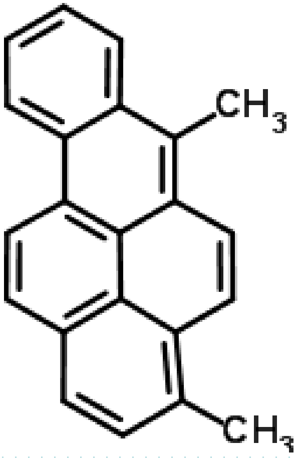
Alkyl PAHs in oil

- Alkyl PAHs in the oil contaminated site are much higher than their unsubstituted/parent PAHs
- Alkyl PAHs are generally more toxic to aquatic life than the parent PAHs

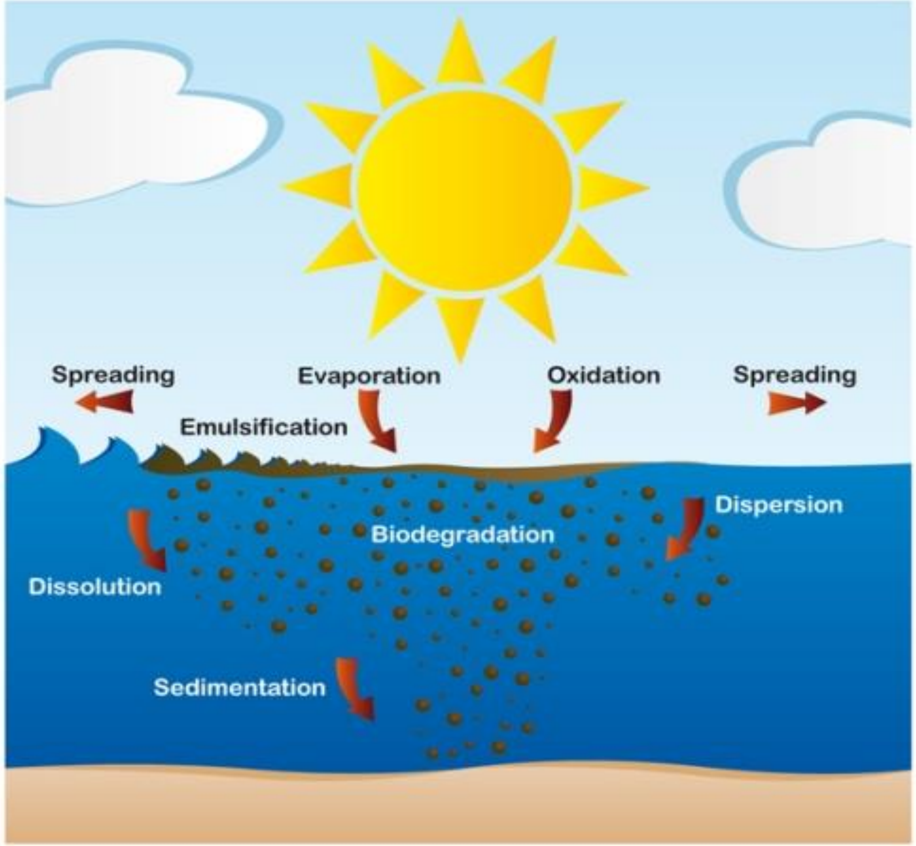








Transport, transformation and weathering of spilled Oil



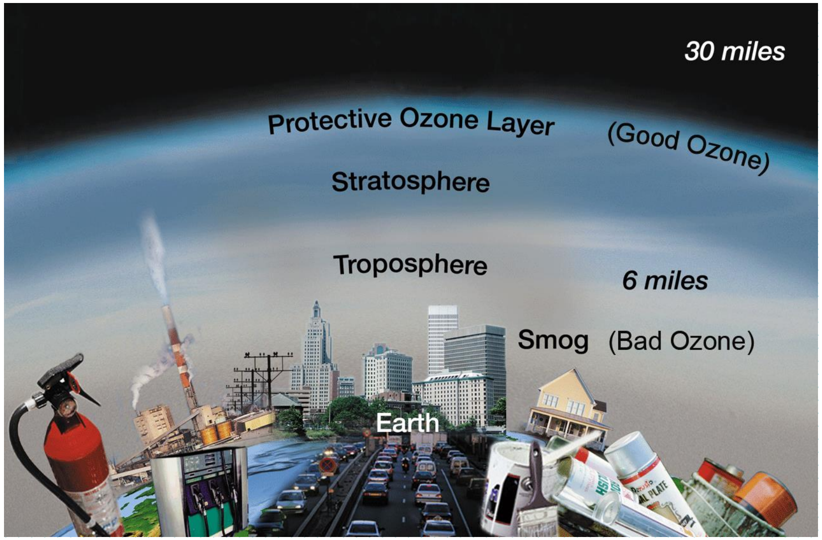
http://educationally.narod.ru/.

Oil weathering due to reaction with atmospheric ozone has been unknown and neglected!

Atmospheric ozone

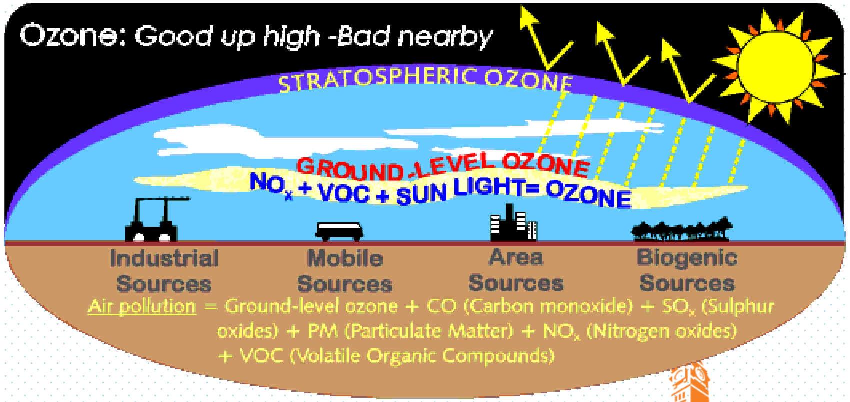
Ozone (O_3):

- Highly reactive, very strong oxidant for organic chemicals (E^0=+2.07 V)
- Toxic to human and plants



Ozone sources:

- Photochemical reactions
- Lightening
- Air pollutants (NOx and VOCs) are key precursors for generating O_3

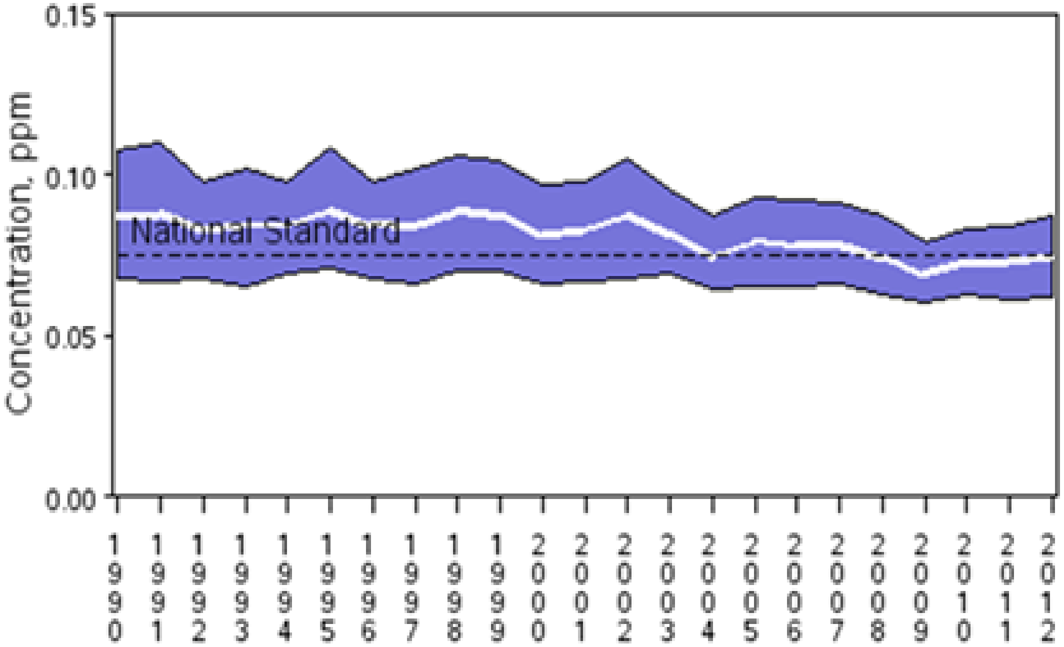


EPA National Ambient Air Quality Standard: 70 ppbv (8-h average)

(Images from: http://www3.epa.gov/apti/ozonehealth/index.html; https://en.wikipedia.org/wiki/Ozone_layer)

Ground-level ozone concentration

- **Based on 2000-2002 data, the 8-h average ozone in Alabama air ranged from 76 to 92 ppb, and the three-year average from 2004 to 2009 ranged from 63 to 86 ppb (ADEM, 2010a; 2010b)**
- **>40 million Americans live with above the 2008 standard of 75 ppbv**
- **Ozone levels over oil slicks can be much higher (Ryerson et al., 2011)**



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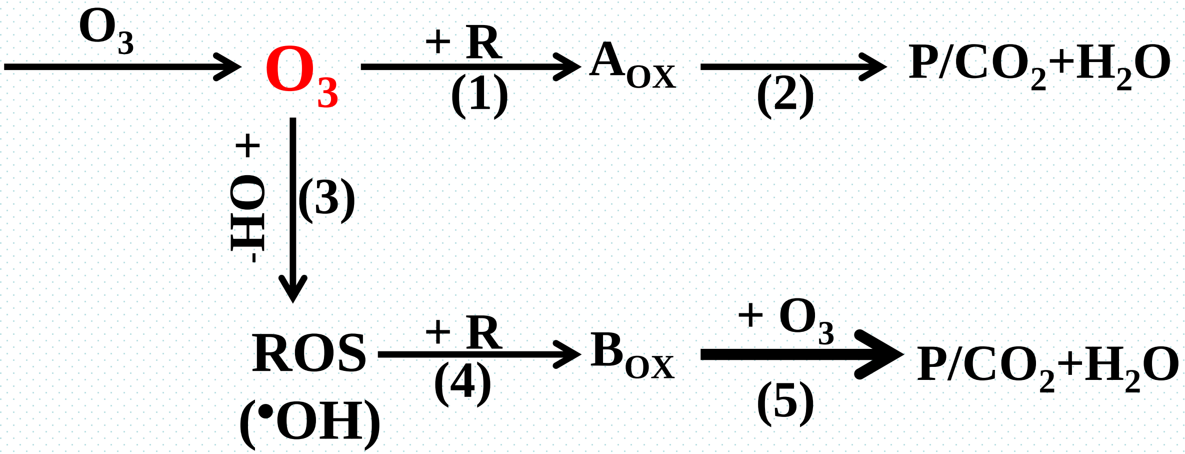
Ozonation Pathways of Oil/PAHs



$$\begin{tikzcd}
{} \arrow[r, "O_3"] & \color{red}{O_3} \arrow[r, "+\ R", "(1)"'] \arrow[d, "(3)", "+\ OH^-"'] & A_{OX} \arrow[r, "(2)"'] & P/CO_2+H_2O \\
{} & \begin{array}{c} ROS \\ (^\bullet OH) \end{array} \arrow[r, "+\ R", "(4)"'] & B_{OX} \arrow[r, Rightarrow, "+\ O_3", "(5)"'] & P/CO_2+H_2O
\end{tikzcd}$$

- Direct ozonation
- Indirect ozonation by $^\bullet$OH radicals ($E^0 = +2.80$ V)

(R: Persistent oil/PAHs; A_{OX} and B_{OX}: Oxidized intermediates by O_3 and •OH, respectively; P: Products; ROS: Reactive oxygen species)

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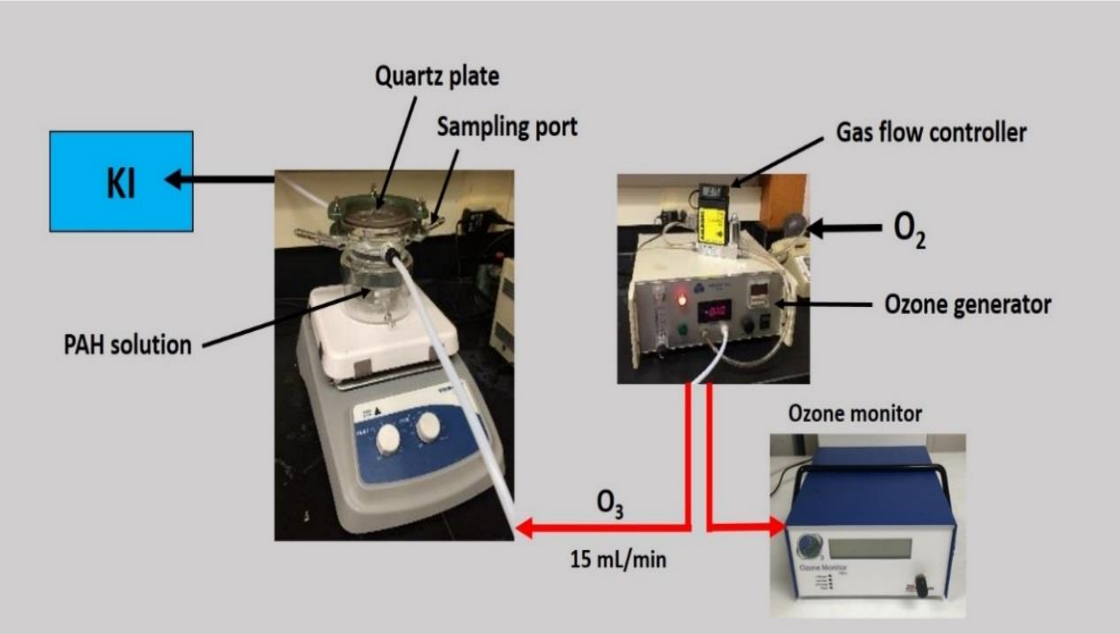
Objectives

- **Determine the rate and extent of simulated natural ozonation of key oil components (PAHs, alkyl PAHs, TPHs, and *n*-alkanes) in seawater**
- **Test effects of model oil dispersants on ozone oxidation of oil components in seawater**
- **Examine effectiveness of ozonation on oxidation of dispersant enhanced water accommodated oil (DWAO)**
- **Elucidate the reaction mechanisms**

Experimental Setup



Left: Schematic of ozone generation and monitoring, and batch ozonation of oil/PAHs.

Key apparatuses: A glass cylinder batch reactor (H×D = 5x8 cm with quartz top), a 2B Tech Ozone Monitor M106-L (2B Technologies, Inc., Colorado), an A2Z Ozone Generator (Model HB5735B, USA), and an Aalborg mass flow controller (Model GFC17, USA)

Right: Close-up of the ozonation reactor. Two ports connected to Teflon tubes for gas flow and two ports sealed by ground glass joints for sample collection. This reactor has a water cooling system, and the quartz top allows for light penetration

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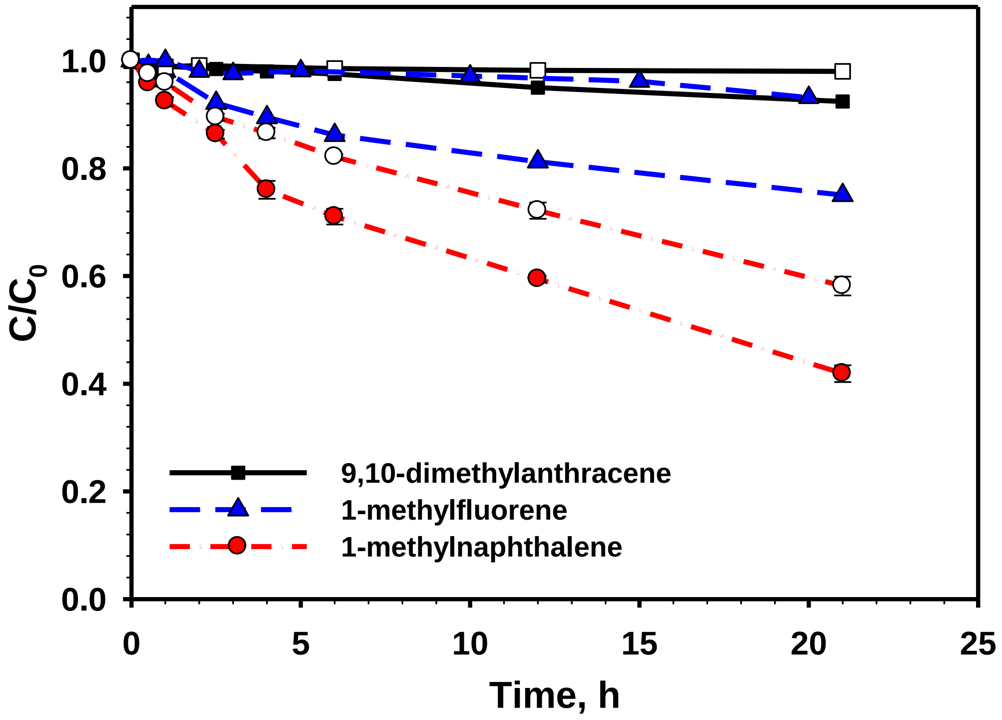
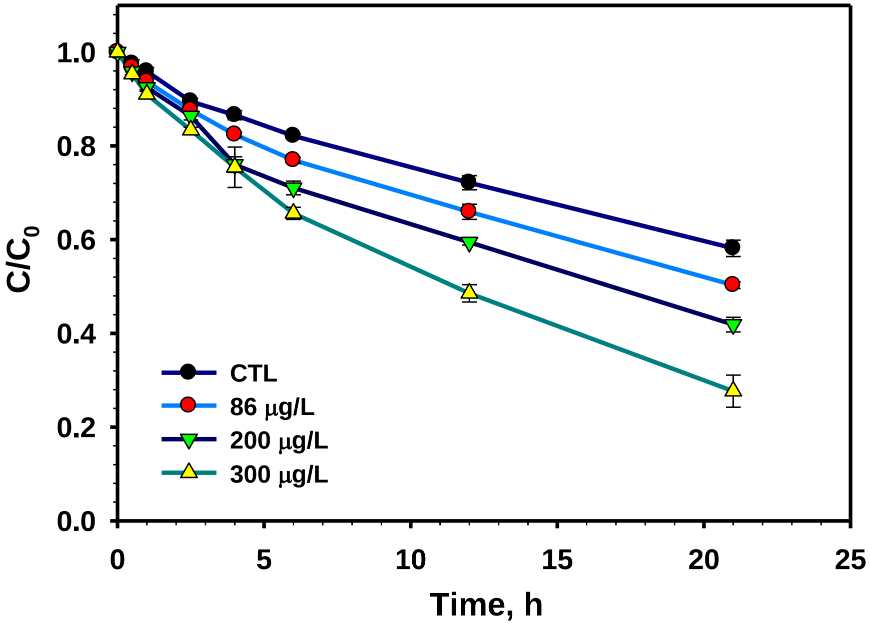
Ozone oxidation of three alkylated PAHs

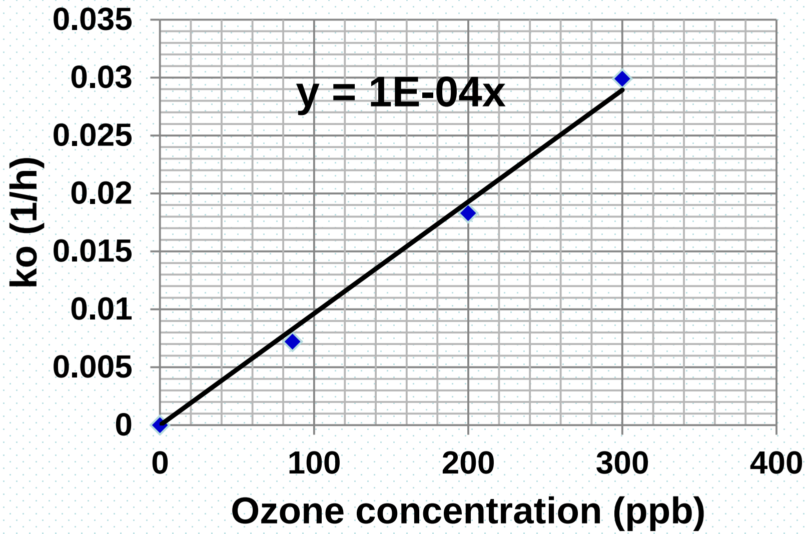


9, 10-dimethylanthracene = 40 µg/L, 1-methylfluorene = 200 µg/L, 1-methylnaphthalene = 500 µg/L, ozone = 200 ppbv, gas flow = 15 mL/min

- 9, 10-dimethylanthracene is less volatile and more stable under surface level ozone than the other two PAHs, which may be due to it highly stable chemical structure, i.e., three fused benzene rings.

Ozonation of 1-methylnaphthalene at various atmospheric ozone levels





Experimental conditions: Initial 1-methylnaphthalene = 500 μg/L, gas flow rate = 15 mL/min, initial pH = 8.3

Ozone (μg/L)	Volatilization		Overall dissipation		Ozonation
	k_v (h^{-1})	R^2	k (h^{-1})	R^2	k_o (h^{-1})
0	0.0249	0.99	0.0249	0.99	0
86	0.0249	0.99	0.0321	0.98	0.0072
200	0.0249	0.99	0.0432	0.96	0.0183
300	0.0249	0.99	0.0548	0.99	0.0299

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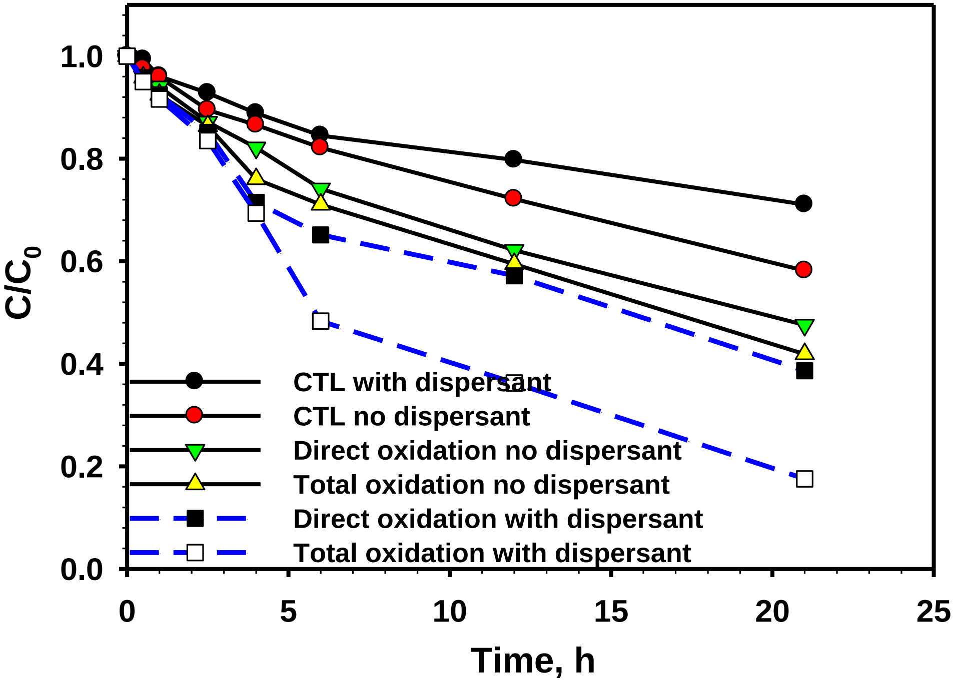
Volatilization and ozone oxidation of 1-methylnaphthalene with or without Corexit 9500A



$$\frac{dC}{dt} = (k_v + k_D + k_R)C$$

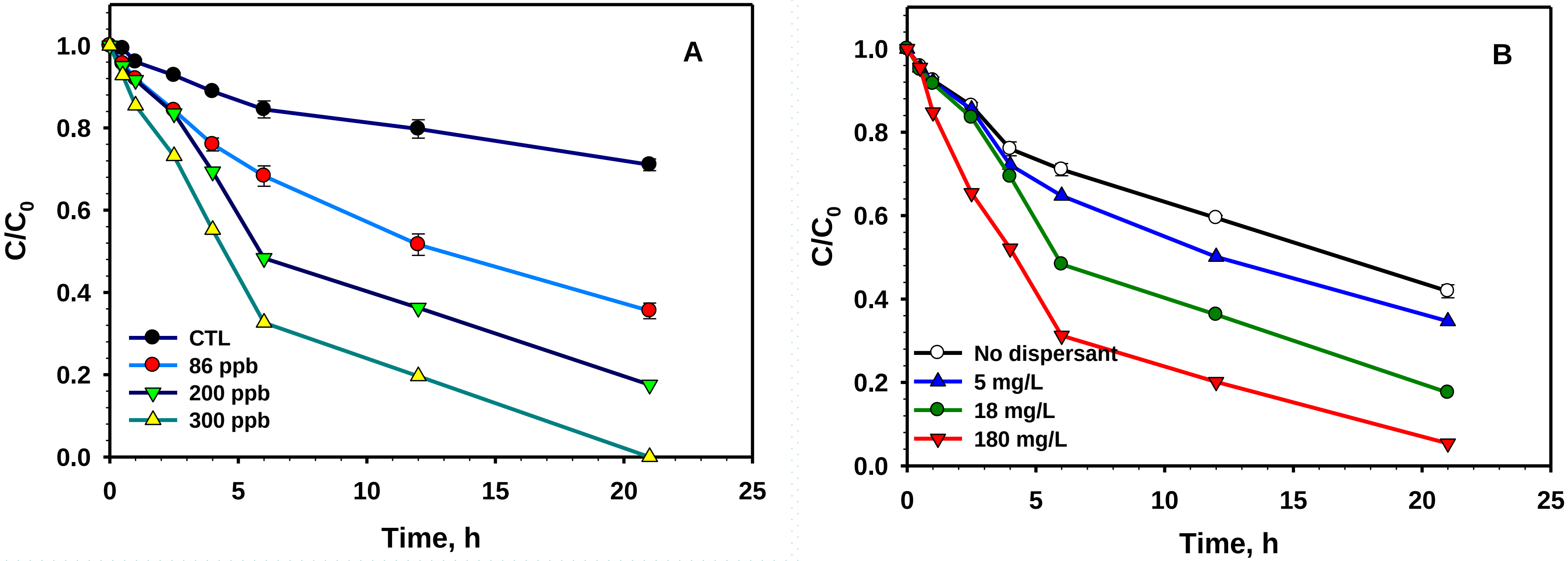
$$k_R = k_o - k_D$$

C: reactant concentration (μg/L)
k: overall depletion rate constant (h^{-1})
k_v: volatilization rate constant (h^{-1})
k_o: overall ozonation rate constant (h^{-1})
k_D: direction ozonation rate constant (h^{-1})
k_R: indirection ozonation rate constant (h^{-1})

- **Dispersant enhances overall degradation**
- **Indirect ozonation becomes more important in the presence of dispersant**

Dispersant (mg/L)	Volatilization		Direct ozonation		Indirect ozonation
	k_v (h^{-1})	R^2	k_D (h^{-1})	R^2	k_R (h^{-1})
0	0.0249	0.99	0.0128	0.95	0.0055
18	0.0208	0.99	0.0208	0.95	0.0376

Effects of ozone concentration and dispersant concentration on volatilization and ozone oxidation of 1-methylnaphthalene



(A) Effects of ozone concentration with 18 mg/L Corexit 9500; (B) Effects of dispersant concentration at ozone of 200 ppbv

- **While the dispersant reduces volatilization loss, it enhances ozonation rate**
- **Dispersant facilitates generation of more free radicals, enhancing indirect ozonation**

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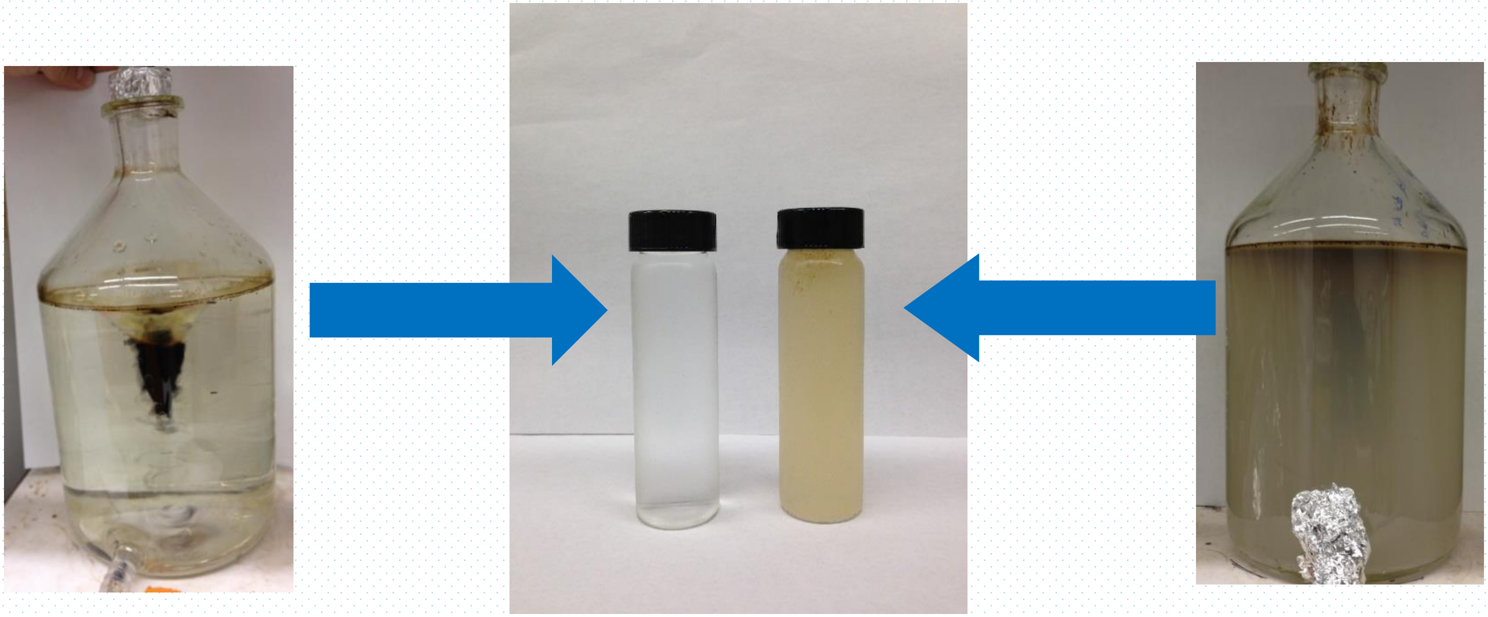
Ozonation of TPHs, PAHs and *n*-alkanes in dispersed oil

Preparation of WAO and DWAO

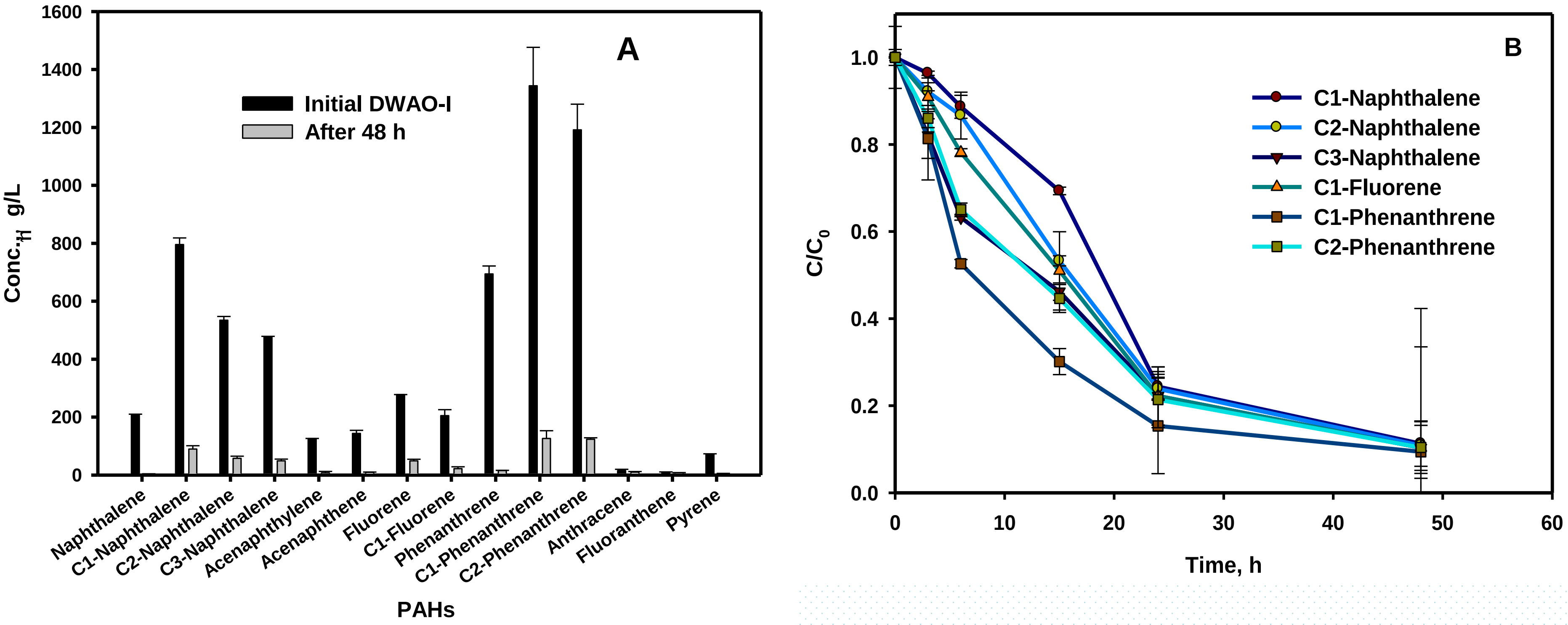


Oil:Seawater = 1:200 (v/v)

Dispersant:Oil:Seawater = 1:20:400 (v/v/v)

- **Water accommodated oil (WAO): 0.79 mg/L TPHs, 0.52 mg/L total PAHs and 0.12 mg/L *n*-alkanes**
- **Dispersant-enhanced WAO prepared with Corexit EC9500A): 149.7 mg/L TPHs, 6.2 mg/L total PAHs and 79.3 mg/L *n*-alkanes**

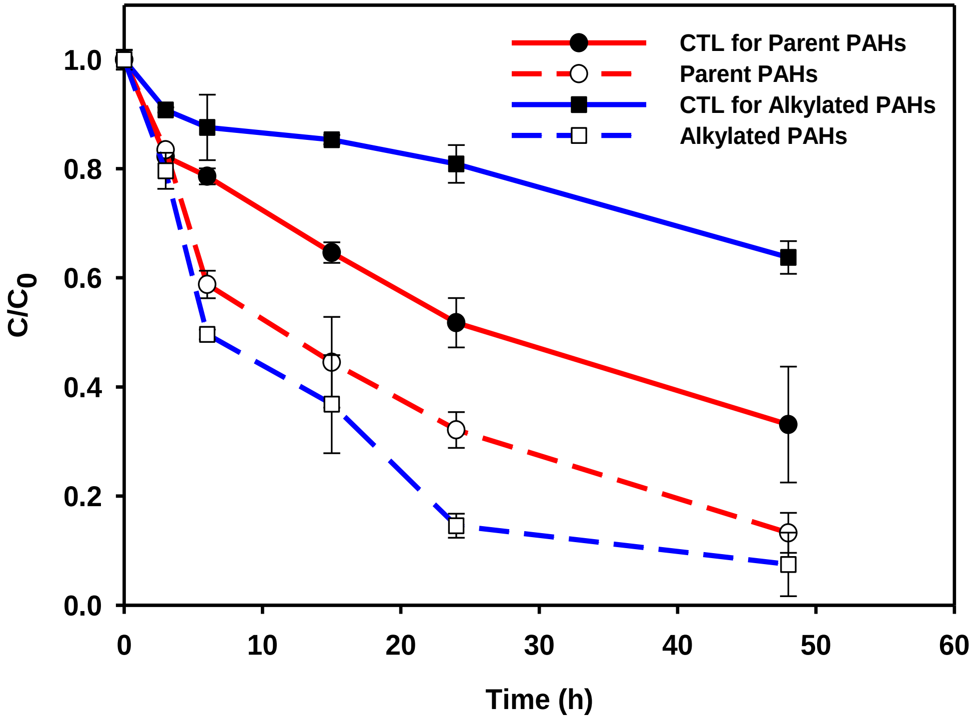
Distribution and ozonation of PAHs in DWAO



- **Initial Parent PAHs in DWAO = 1.34 mg/L**
- **Initial Alkylated PAHs in DWAO = 4.82 mg/L**
- **Naphthalene and phenanthrene and their alkylated compounds are most abundant**
- **C1-Phen shows the fastest ozonation rate, while C1-Naph the slowest**
- **Nearly 90% all PAHs degraded in two days**

Experimental conditions: Ozone = 86 ppbv, salinity = 2%, gas flow = 15 mL/min

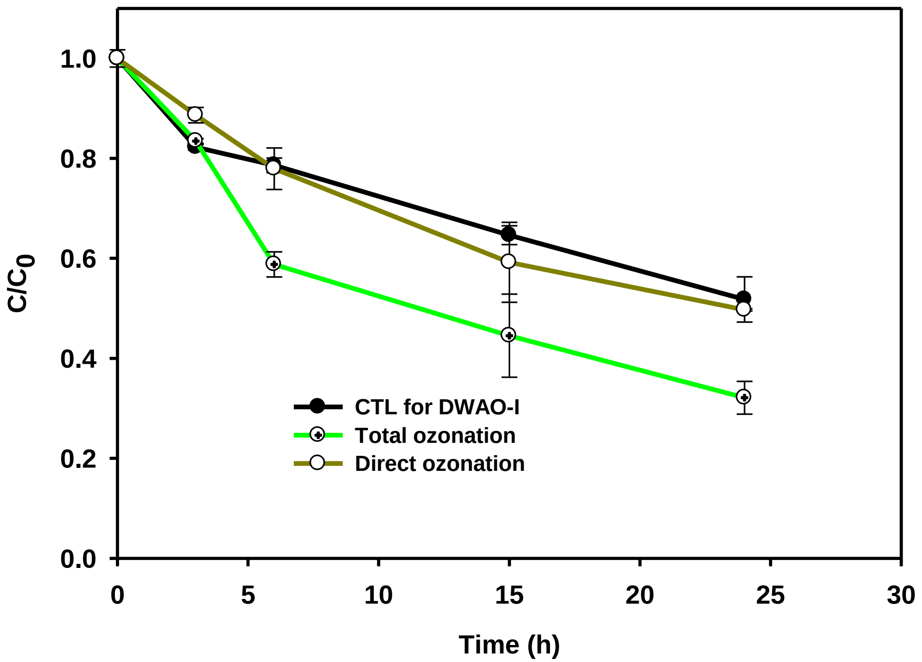
Ozonation of parent and alkyl PAHs in DWAO

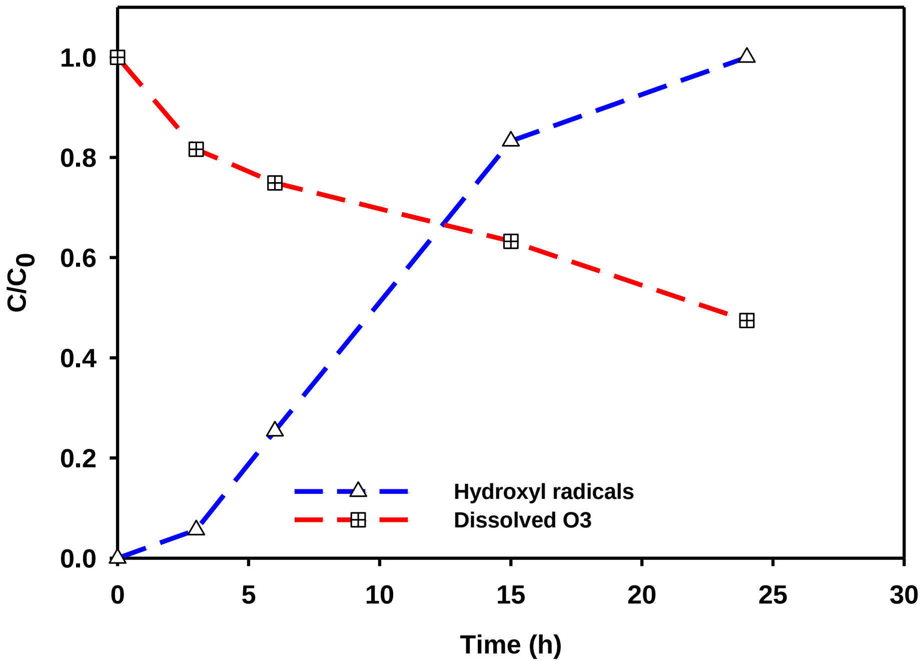


- Alkylated PAHs are more prone to ozonation. After 48 h, >92.5% of alkylated PAHs was depleted, compared to 86.7% of Parent PAHs
- k_o (h^{-1}) of alkylated PAHs 1.4 times higher than that of Parent PAHs

Type	Volatilization		Overall dissipation		Ozonation
	k_v (h^{-1})	R^2	k (h^{-1})	R^2	k_o (h^{-1})
Total PAHs	0.0146	0.9642	0.3528	0.9655	0.3382
Parent PAHs	0.0237	0.9703	0.2823	0.9625	0.2586
Alkylated PAHs	0.0082	0.9349	0.3720	0.9677	0.3638

Direct vs. indirect ozonation of PAHs in DWAO and evolution of dissolved O_3 and $^{\bullet}OH$ radicals

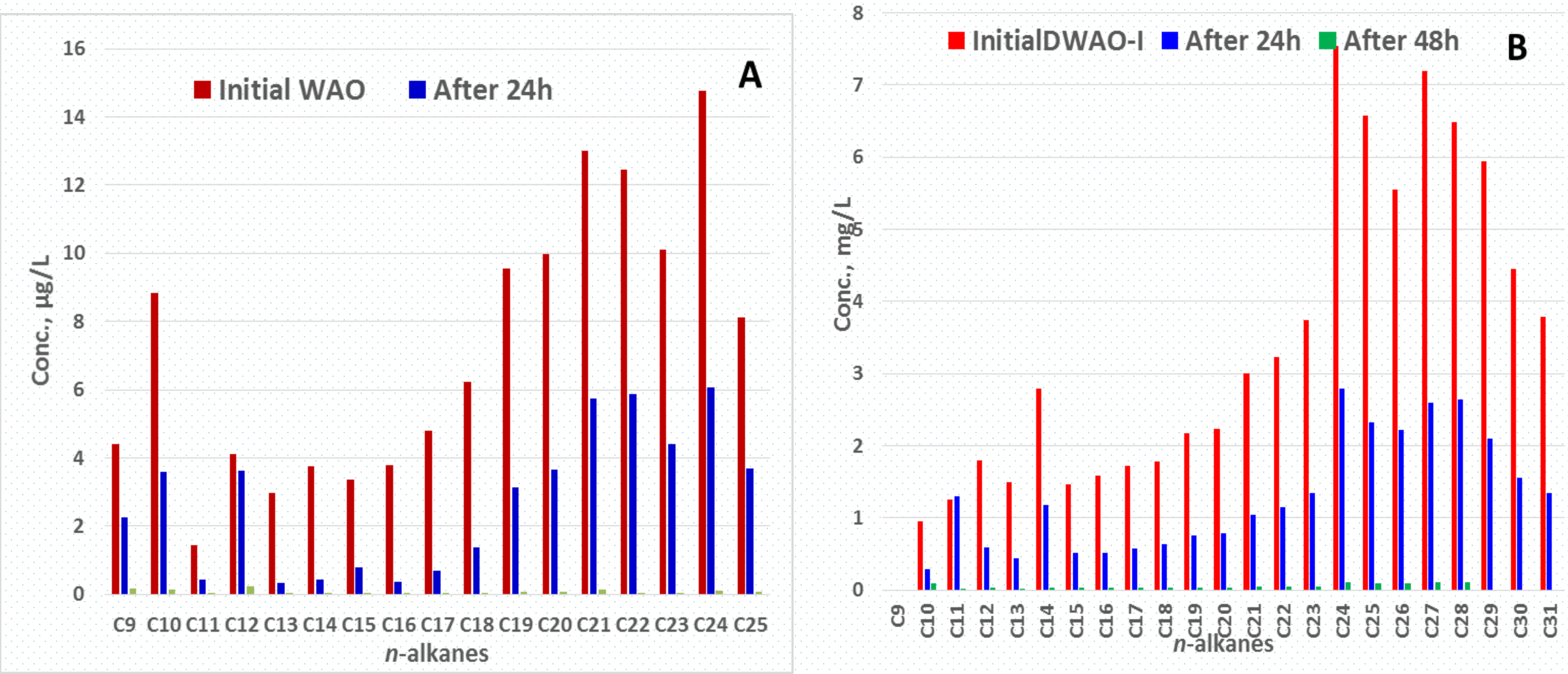




- Indirect ozonation rate is 2.7 times faster than direct ozonation
- DWAO favors generation of radicals

Type	Volatilization		Overall dissipation		Ozonation		
	k_v (h^{-1})	R^2	k (h^{-1})	R^2	k_O (h^{-1})	k_R (h^{-1})	k_D (h^{-1})
Total ozonation	0.0237	0.9703	0.0510	0.9625	0.0264	0.0193	0.0071
Direct ozonation	0.0237	0.9703	0.0361	0.9564	0.0071	0	0.0071

Distribution and ozonation of *n*-alkanes in WAO and DWAO



- **Corexit EC9500A increased concentration of *n*-alkanes from 0.12 to 79.3 mg/L, especially the larger *n*-alkanes**
- **Ground-level ozone plays an important role in weathering of dispersed *n*-alkanes**

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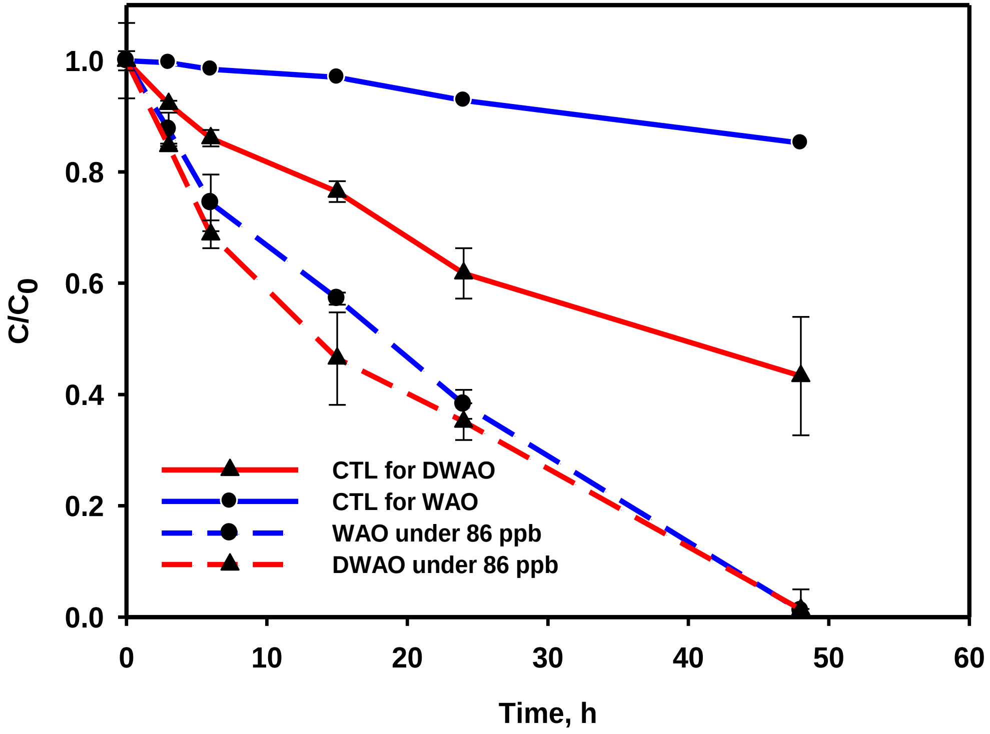
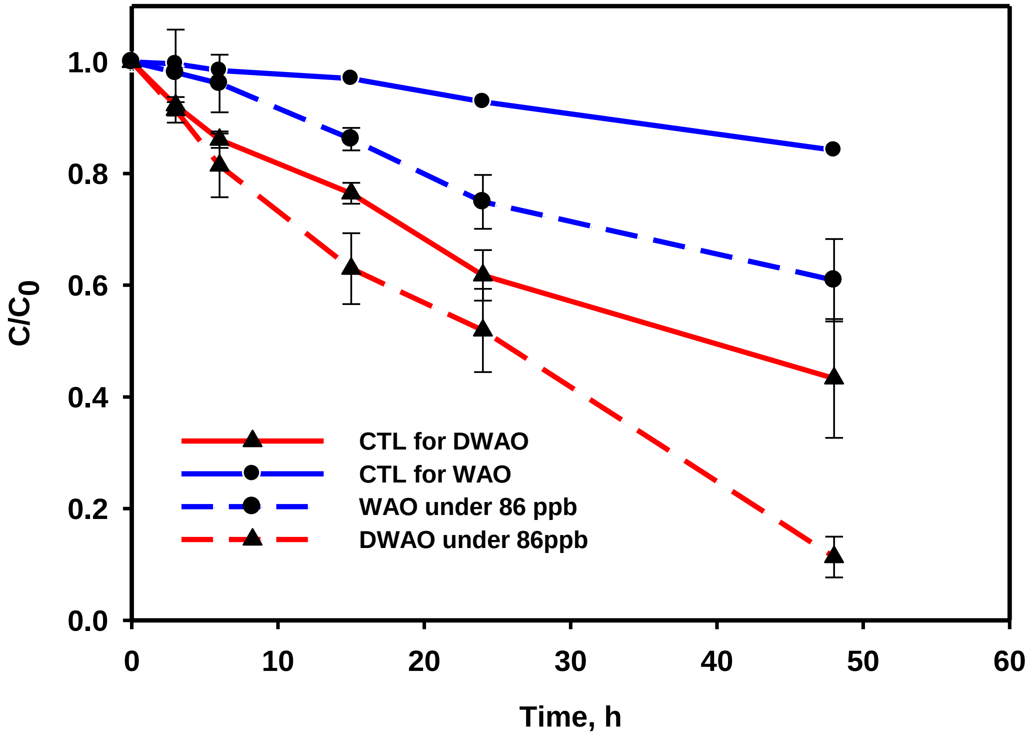
Ozonation of *n*-alkanes in WAO and DWAO



- **Initial *n*-alkanes in WAO and DWAO = 0.12 and 79.3 mg/L, O_3 = 86 ppbv**
- **Nearly complete depletion of *n*-alkanes in two days**

Type	Volatilization		Overall dissipation		Ozonation
	k_v (h^{-1})	R^2	k (h^{-1})	R^2	k_o (h^{-1})
WAO	0.0034	0.9856	0.0445	0.9742	0.0411
DWAO	0.0177	0.9920	0.0510	0.9835	0.0333

Ozonation of TPHs in WAO and DWAO



- Initial TPHs concentration in WAO and DWAO = 0.79 and 149.7 mg/L
- For DWAO, volatilization rate ≈ ozonation rate; For WAO, ozonation > volatilization
- Ozonation in DWAO >2 times faster than in WAO

Type	Volatilization		Overall dissipation		Ozonation
	k_v (h^{-1})	R^2	k (h^{-1})	R^2	k_o (h^{-1})
WAO	0.0036	0.9813	0.0109	0.9895	0.0073
DWAO	0.0177	0.9920	0.0337	0.9752	0.0160

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Part I Summary

- Atmospheric ozone plays a significant role in oil weathering
- Oil dispersants enhances ozonation of oil hydrocarbons due to elevated generation of reactive radicals
- Indirect ozonation becomes the more important mechanism in DWAO

Photochemical degradation of PAHs and dispersed oil in seawater: Effects of dispersants

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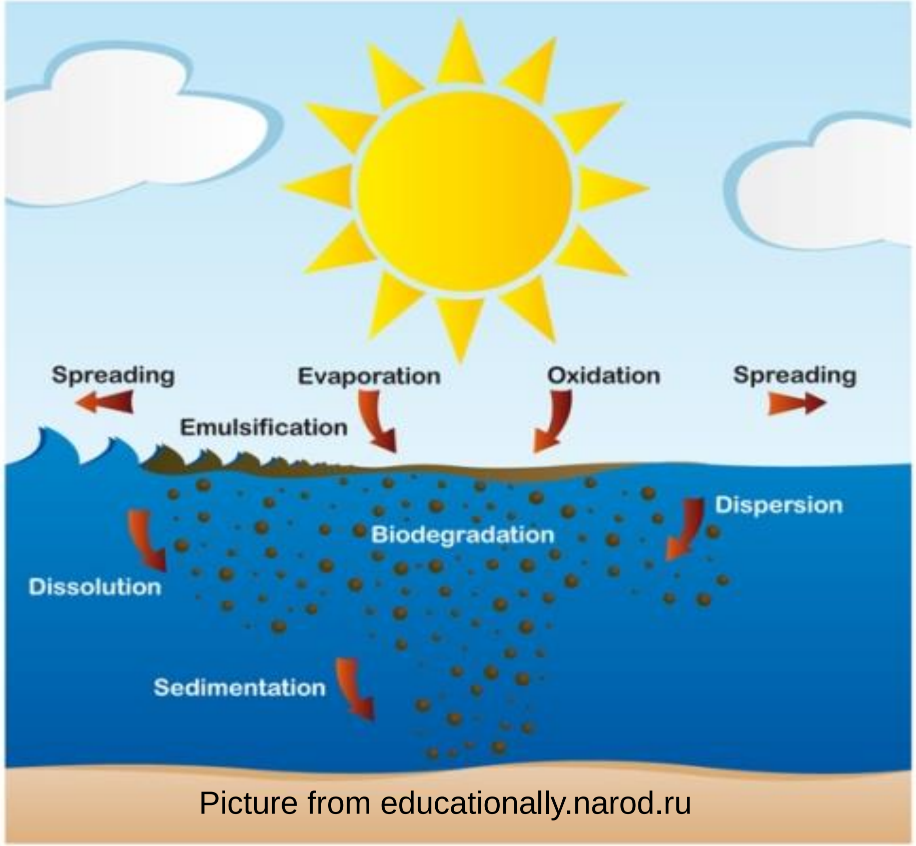
Fate of Spilled Oil



Picture from educationally.narod.ru

How oil dispersant affect the photodegradation of spilled oil, especially alkylated PAHs?

Materials and Methods

Newport 94041A solar simulator with a 450W xenon-zone free short arc lamp with an air mass filter

Photoreactor with cooling water coat and quartz cover

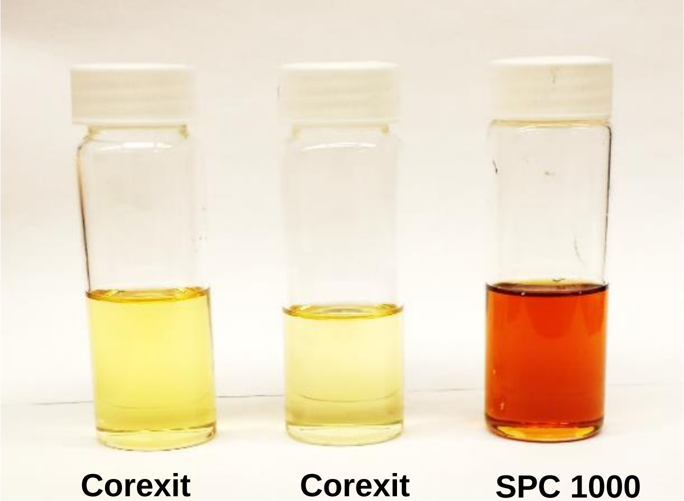
Materials and Methods

- **Seawater**
  - **Filtered through 0.45 μm membrane filters**
  - **Sterilized through autoclaving**
  - **Measured for pH, salinity, and DOC (pH = 8.0, salinity = 3.1%, DOC = 0.43 mg/L)**
- **PAHs**
  - **Napthalene, 1-methylnaphthalene**
  - **Anthracene, 9,10-dimethylanthracene**

Sampling site:
Grand Bay

Materials and Methods

Tested dispersants

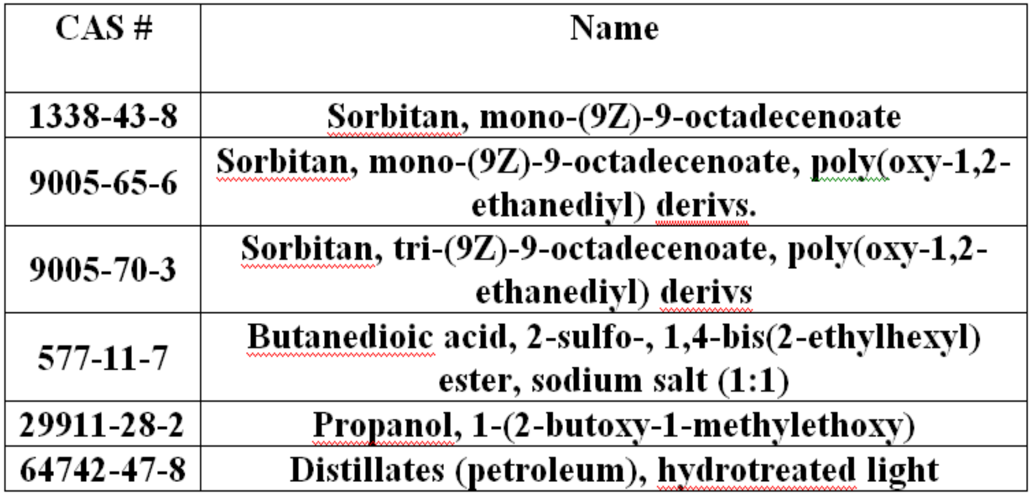


Corexit EC9500A

Corexit EC9527A

SPC 1000

Compositions of Corexit EC9500A



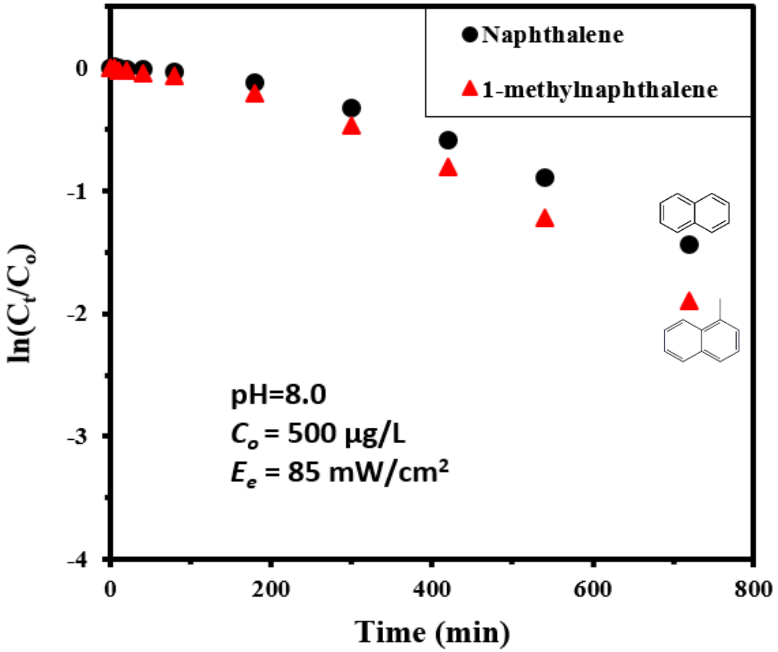
CAS #	Name
1338-43-8	Sorbitan, mono-(9Z)-9-octadecenoate
9005-65-6	Sorbitan, mono-(9Z)-9-octadecenoate, poly(oxy-1,2-ethanediyl) derivs.
9005-70-3	Sorbitan, tri-(9Z)-9-octadecenoate, poly(oxy-1,2-ethanediyl) derivs
577-11-7	Butanedioic acid, 2-sulfo-, 1,4-bis(2-ethylhexyl) ester, sodium salt (1:1)
29911-28-2	Propanol, 1-(2-butoxy-1-methylethoxy)
64742-47-8	Distillates (petroleum), hydrotreated light

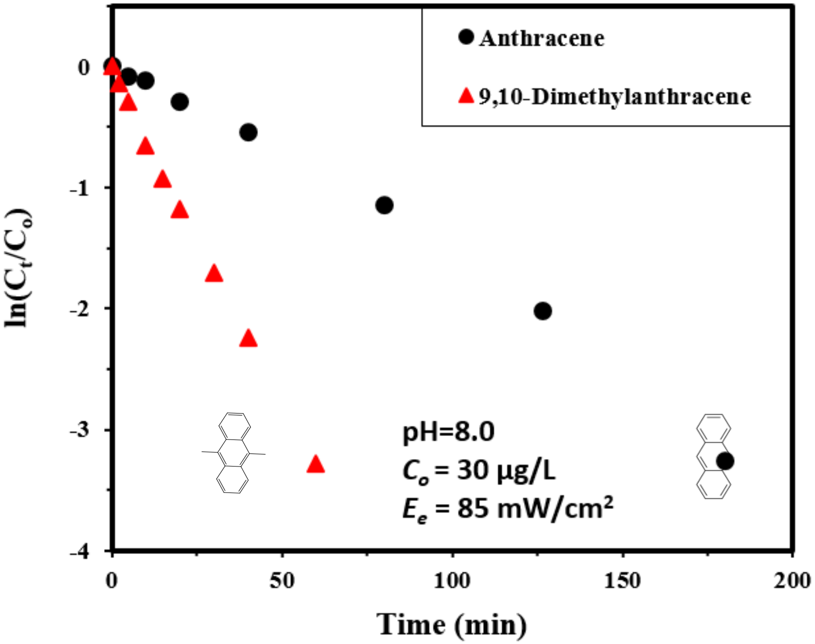
Nonionic surfactants: Ethoxylated sorbitan monooleate, ethoxylated sorbitan trioleate and sorbitan monooleate

Anionic surfactants: Sodium dioctyl sulfosuccinate

Hydrocarbon solvent: Ethylene glycol monobutyl ether

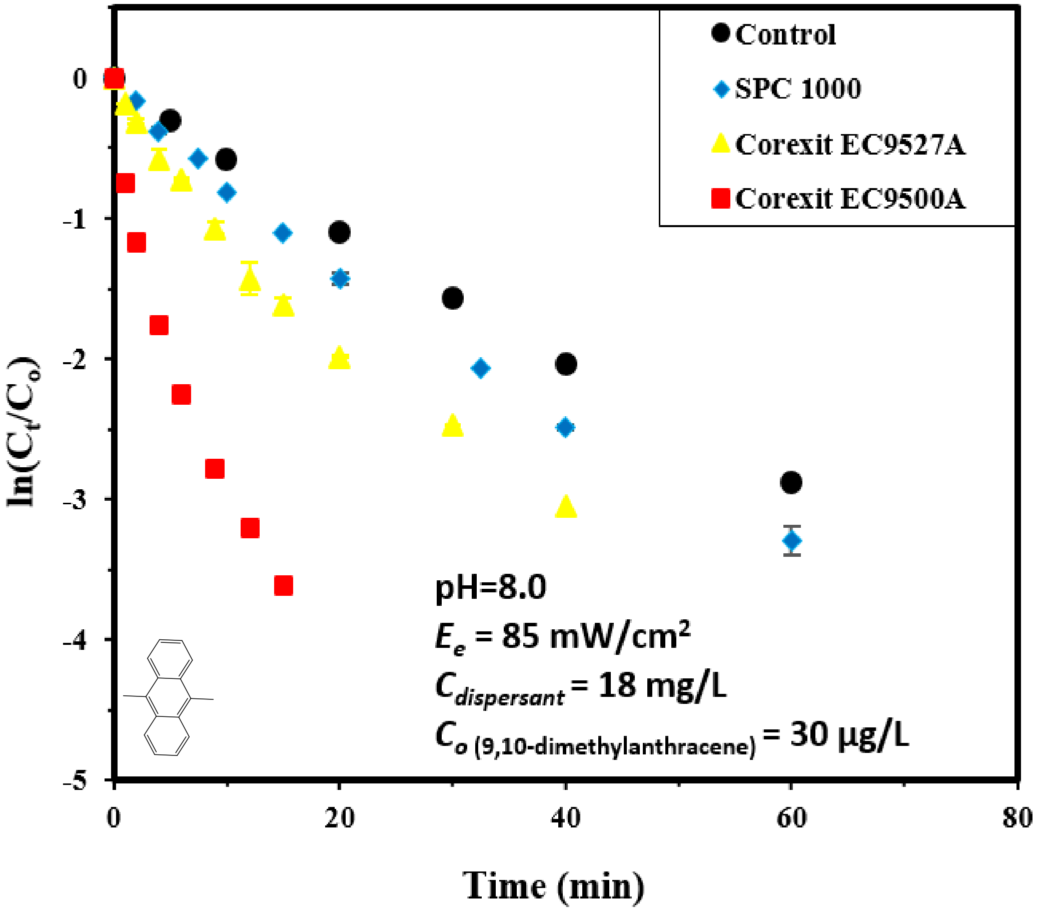
Photolysis of Various PAHs in Seawater





- Both two-ring and three-ring PAHs are prone to photodegradation
- Alkylated PAHs are more photodegradable than their parent PAHs

Effects of Three Dispersants on Photolysis of 9,10-dimethylanthracene



All three dispersants accelerate the photolysis rate of 9,10-dimethylanthracene

Corexit EC9500A is most effective

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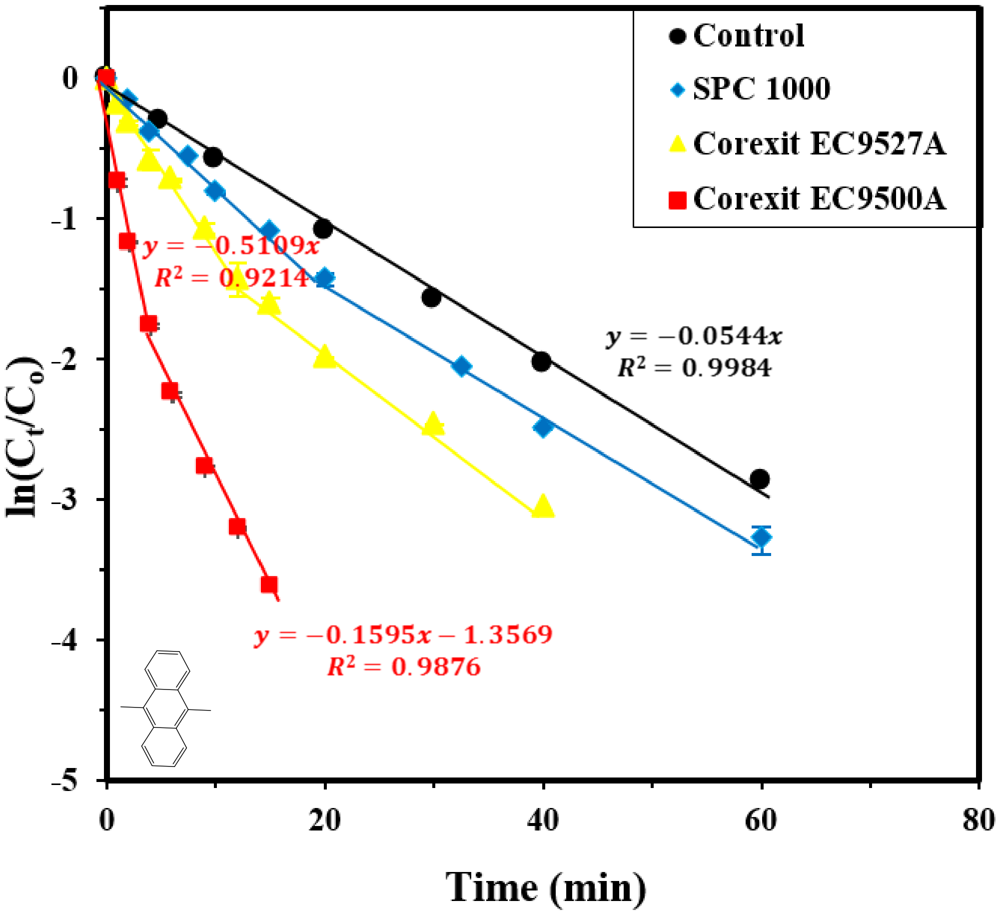
Effects of Three Dispersants on Photolysis of 9,10-dimethylanthracene



$$\ln(C/C_0) = -kt$$

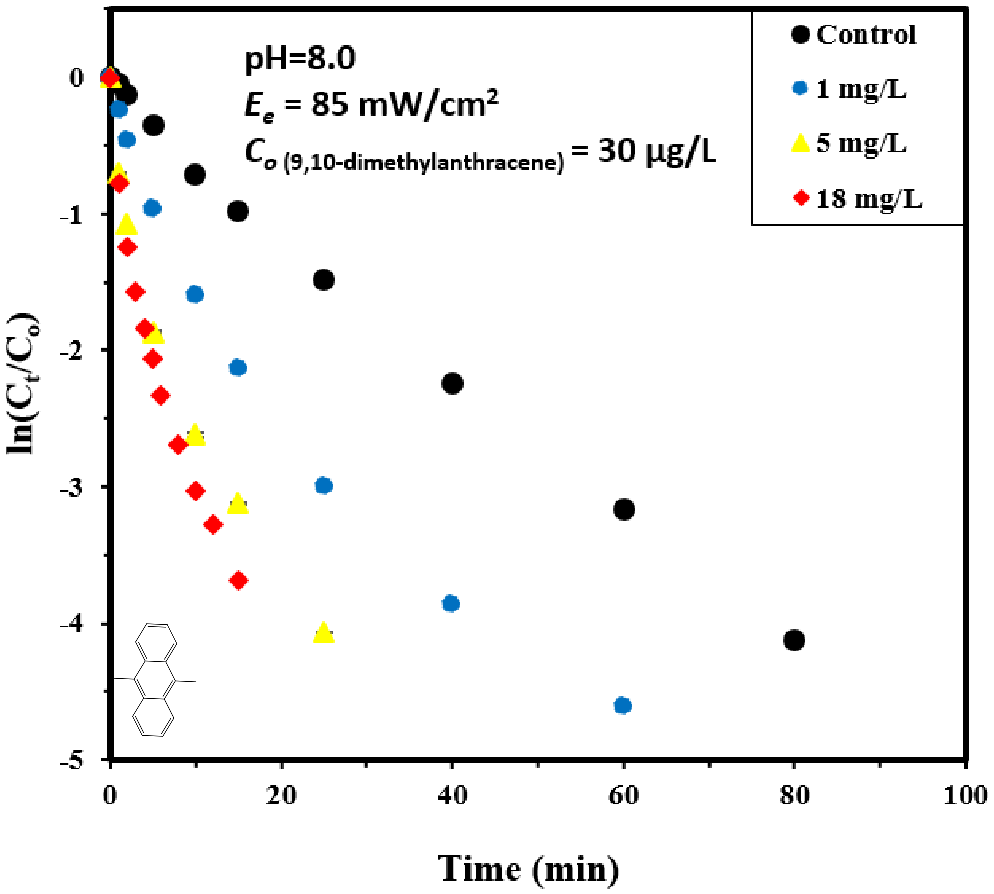
C: **Reactant concentration at *t***
C_0: Reactant concentration at *t*=0
k: **Rate constant**

All three dispersants accelerate the photolysis rate

Corexit EC9500A is most effective

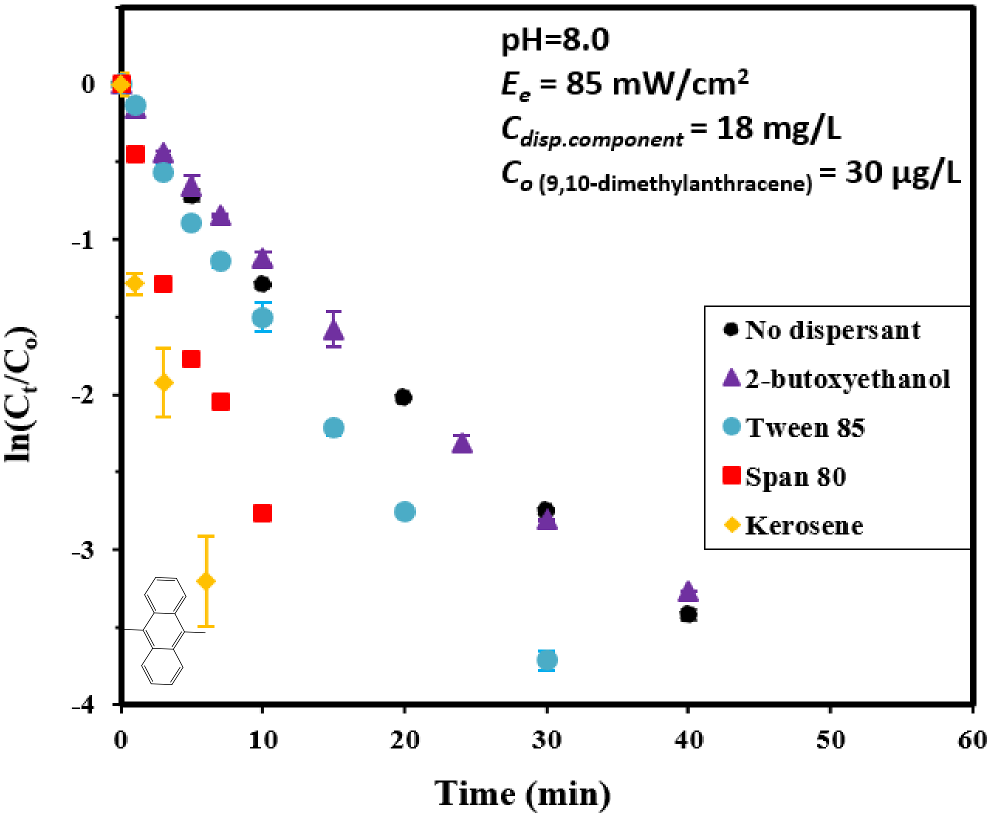
A 2-stage kinetic profile is observed with dispersants

Effects of Dispersant Concentration on Photolysis of 9,10-dymethylanthracene



- The photolysis rate increases proportionally with increasing dispersant concentration in the dispersant range of 0-5 mg/L
- Less increase at dispersant > 5 mg/L

Effects of Individual Dispersant Components on Photodegradation of 9,10-dimethylanthrancene



	k (min^{-1})	R^2
No dispersant	0.0824	0.9826
2-butoxyethanol	0.083	0.9844
Tween 85	0.1248	0.9872
Span 80	0.2675	0.9654
Kerosene	0.4875	0.9373

- ➢ **The effectiveness follows the order: Kerosene > Span 80 > Tween 85**
- ➢ **The non-ionic surfactants are very effective**
- ➢ **Insoluble solvent (kerosene) is very effective while 2-butoxyethanol shows little effect**

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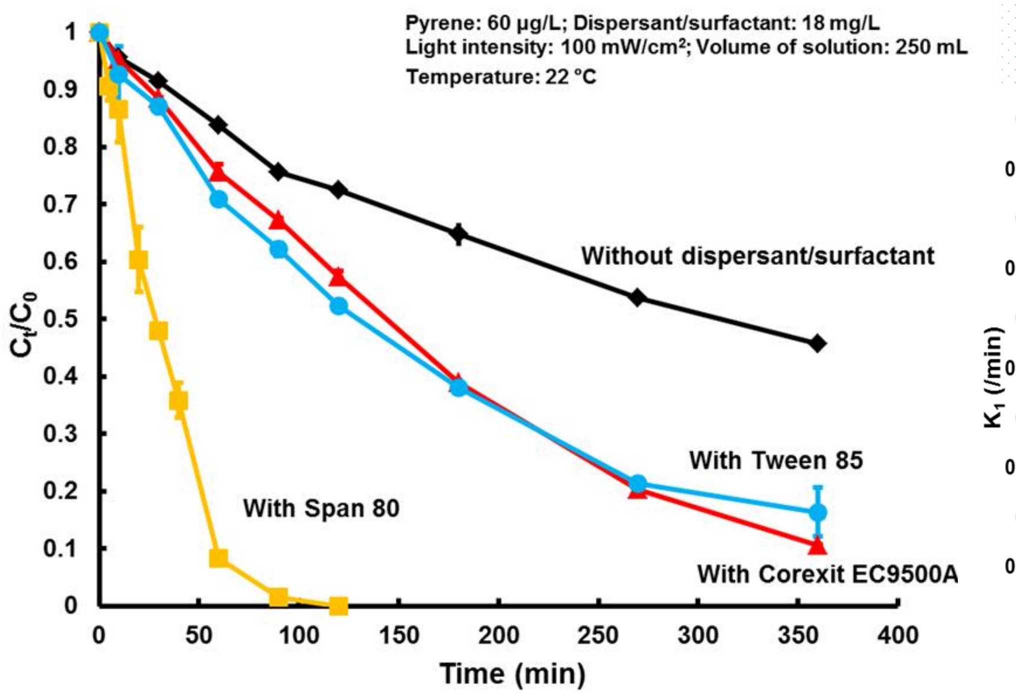
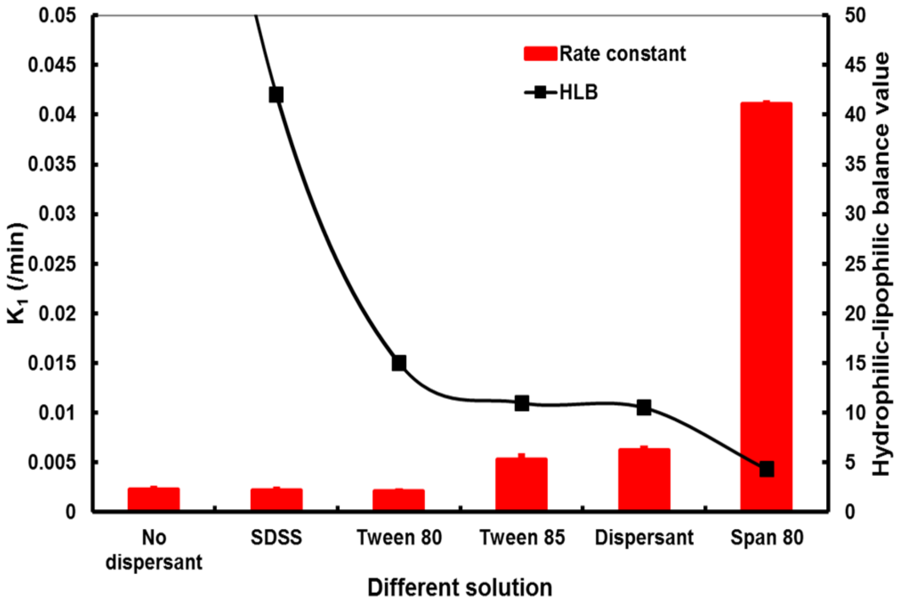
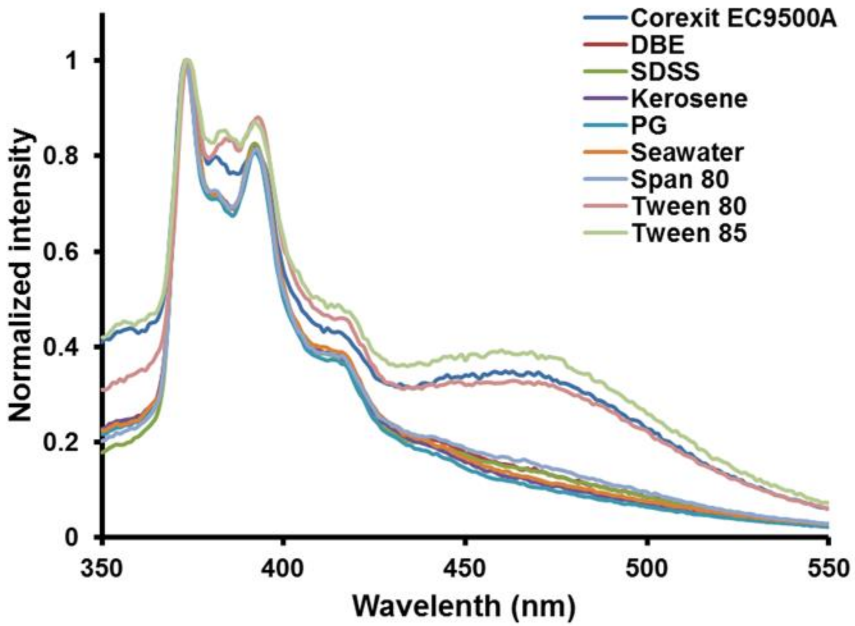
Effects of Individual Dispersant Components on Photodegradation of Pyrene

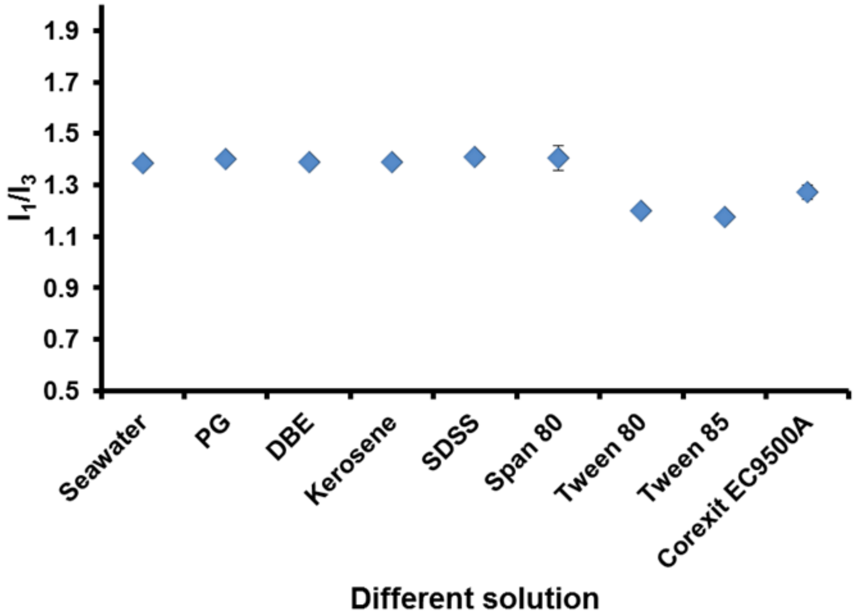




- **Span 80 and Tween 85 increased the rate constant from 0.002 min^{-1} to 0.041 and 0.005 min^{-1}, respectively**
- **The dispersant components with low hydrophilic-lipophilic balance (HLB) values promote pyrene photolysis**

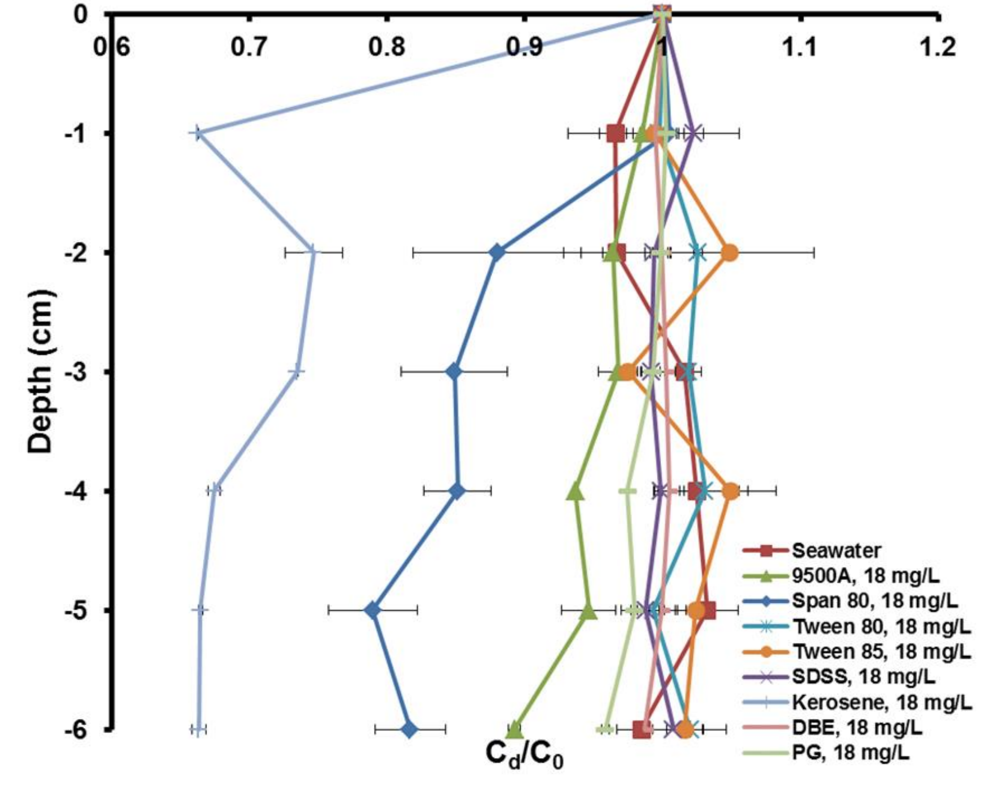
Mechanisms of Surfactant-Enhanced Photodegradation of Pyrene Based on UV-Vis and Fluorescence Spectroscopic Studies





- ➢π electronic cloud of pyrene is disturbed by the sorbitan head groups
- ➢Pyrene is likely to be incorporated into the palisade layer of the micelle
- ➢Pyrene excimers detected in dispersant solution
- ➢High local concentrations of pyrene were observed

Vertical Distribution of Pyrene in Water Column in the Presence of Corexit 9500A and its Components



- **In the presence of dispersant, the concentration of pyrene at the surface layer is 11% higher than that at the bottom**
- **Span 80 and kerosene contributed most**
- **Concentrating PAH at the surface is beneficial for enhanced photodegradation**

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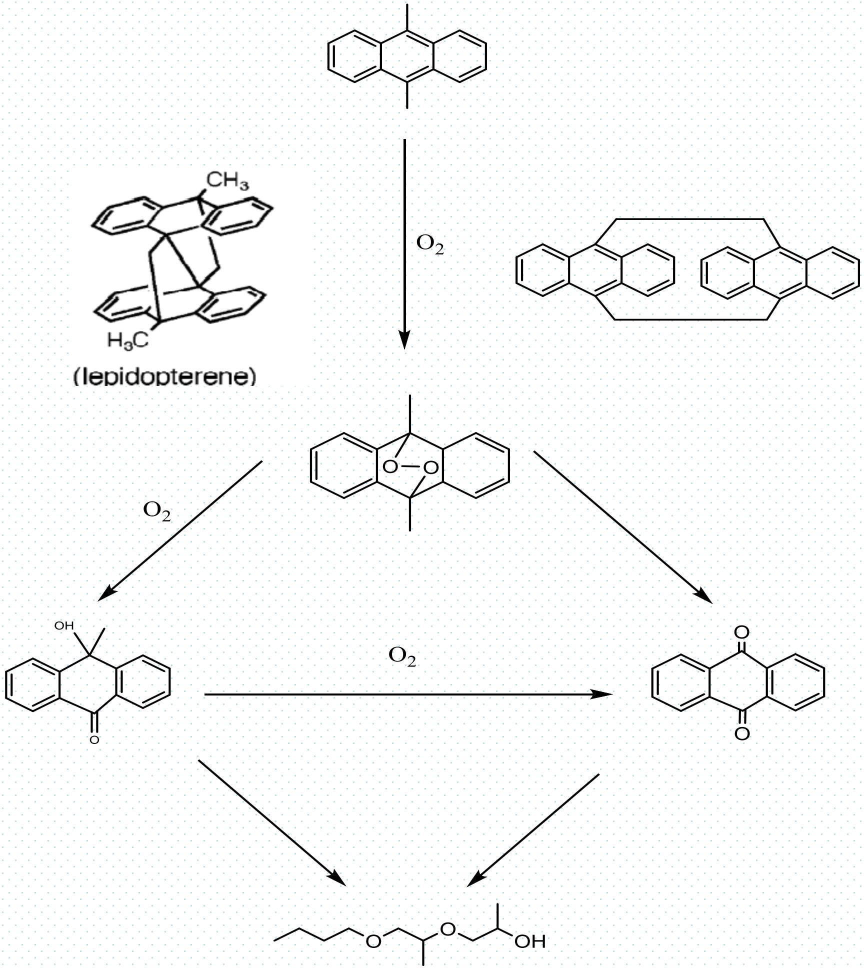
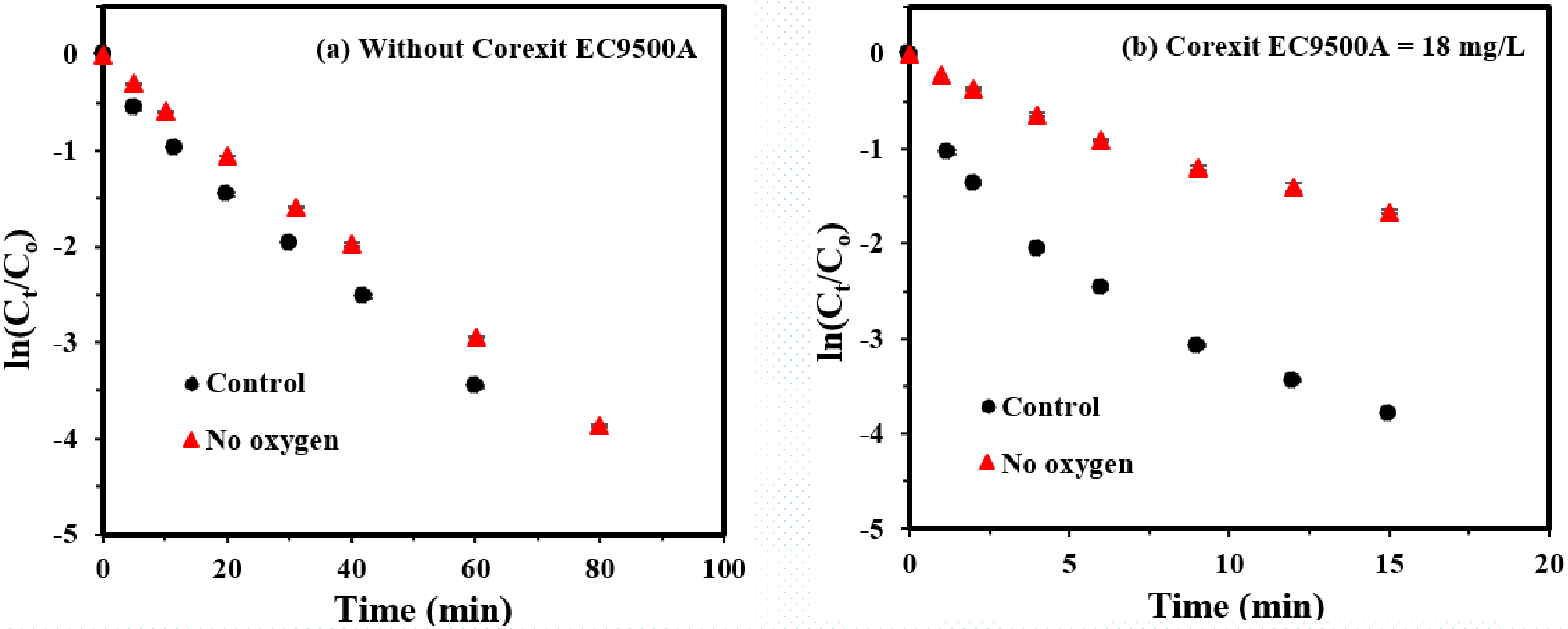
Effects of Dispersant on Photolysis Pathway



Experimental:
Samples were extracted by dichloromethane for three consecutive times, and dewatered and concentrated, and then analyzed by GC/MS.

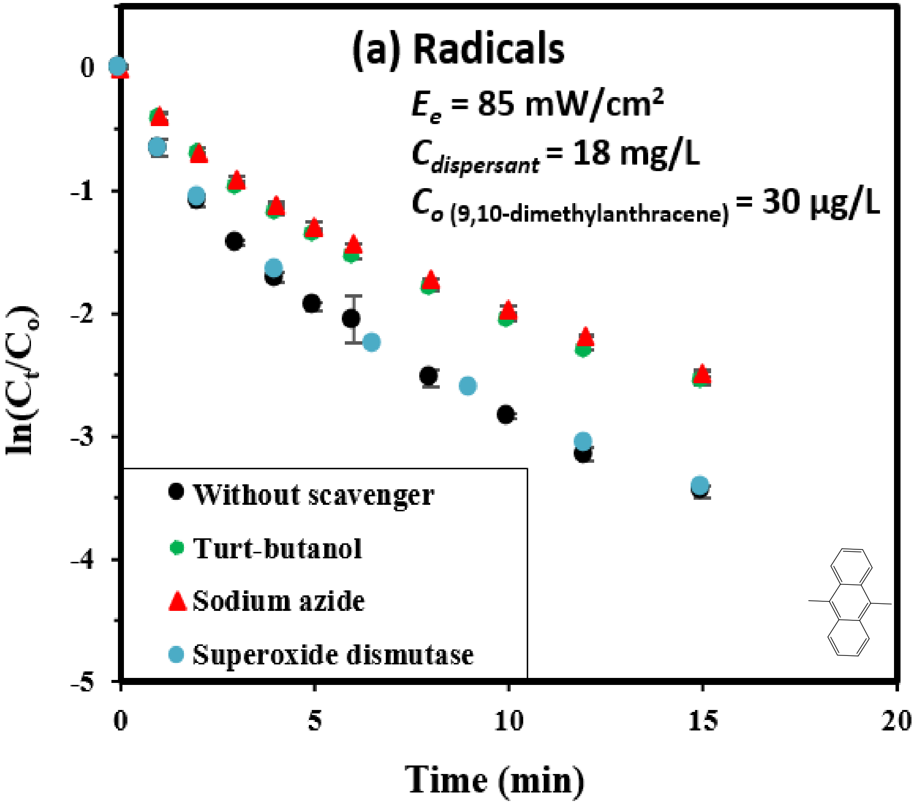
Results:
Corexit EC9500A does not alter the reaction pathway

Effects of DO on Photolysis of 9,10-dimethylanthracene



- In the absence of dispersant, the degradation rate without DO is 17% slower than with DO
- In the presence of dispersant, the reaction rate without DO is 60% slower than with DO
- The presence of dispersant greatly promotes indirect photolysis

Effects of Radicals on Photodegradation of 9,10-dimethylanthrancene



Scanvengers:
Turt-butanol scavenges hydroxyl radicals (•OH)
Sodium azide quench hydroxyl radicals (•OH) and singlet oxygen ($^1O_2$)
Superoxide dismutase for superoxide.

- **Hydroxyl radicals play a key role**
- **Singlet oxygen and superoxide have little effect**

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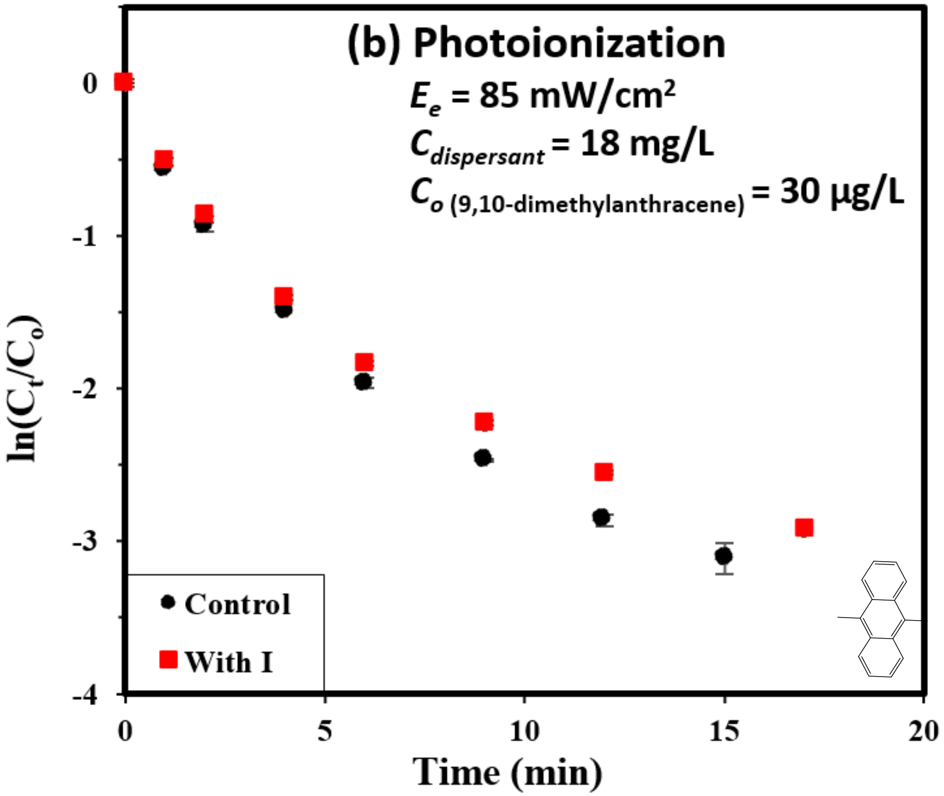
Effects of Photoionization on Photodegradation of 9,10-dimethylanthrance



I^- is applied as a sacrificial electron donor to test the effect of photoionization

Photoionization is important for the photolysis process in the presence of Corexit EC9500A

Part II Summary

- All three dispersants accelerate photochemical degradation of 9,10-dimethylanthracene, with Corexit EC9500A being most effective
- The nonionic surfactants (Tween and Span) are most abundant dispersant components and are most influential in enhancing the photodegradation rate
- DO and Corexit EC9500A may work synergistically to enhance the photochemical reaction rate
- Hydroxyl radicals play an important role in the degradation of 9,10-dimethylanthracene

Acknowledgments

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BOEM
Bureau of Ocean Energy Management