Light-Induced Transformations of the C_{60} Derivative, Fullerenol: Interactions with Natural Organic Matter

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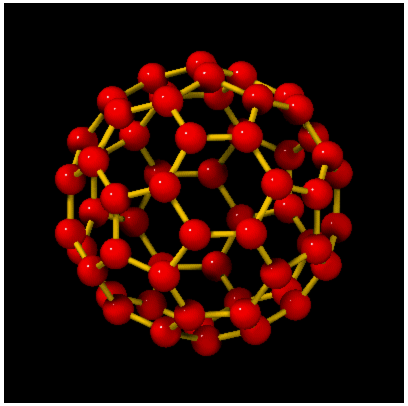
Outline

- Background
- Direct photolysis of fullerenol
- NOM effects on C60 and fullerenol photoreactions
- Spectral studies of NOM and fullerenol
- ROS reactions with fullerenol: $^1O_2$, OH

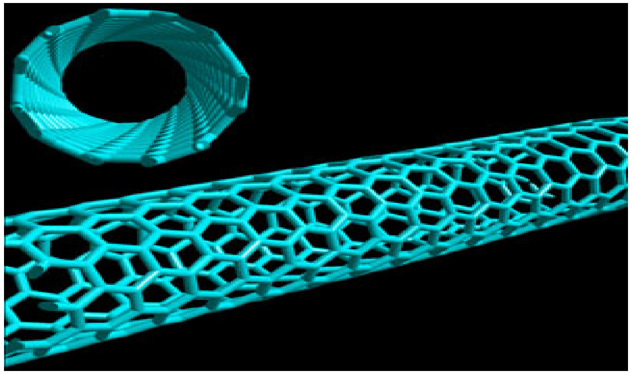
Definition of Fullerenes

- **Fullerenes** are a family of carbon allotropes, molecules composed entirely of carbon, in the form of a hollow sphere, ellipsoid, tube, or plane . Spherical fullerenes are also called **buckyballs**, and cylindrical ones are called carbon nanotubes or **buckytubes**.

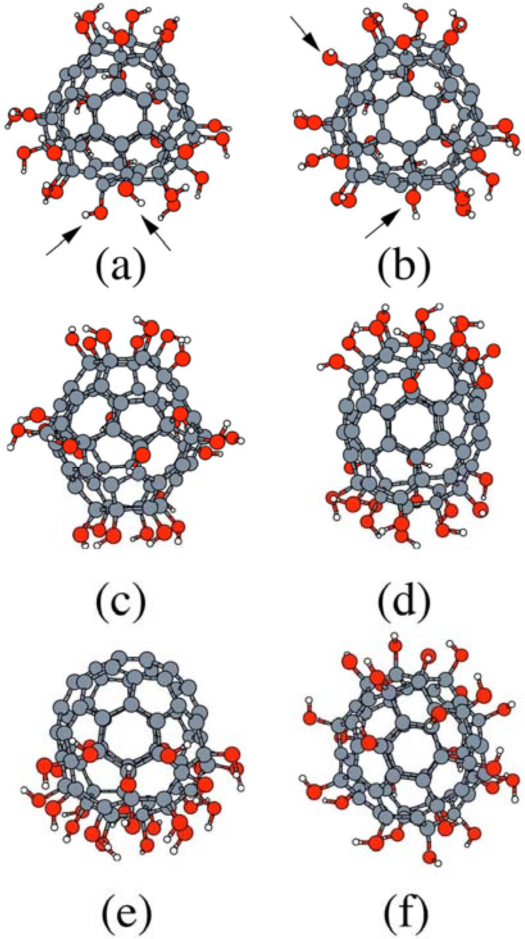
Molecular Structures of Carbon Nanomaterials (Fullerenes)



C_{60}

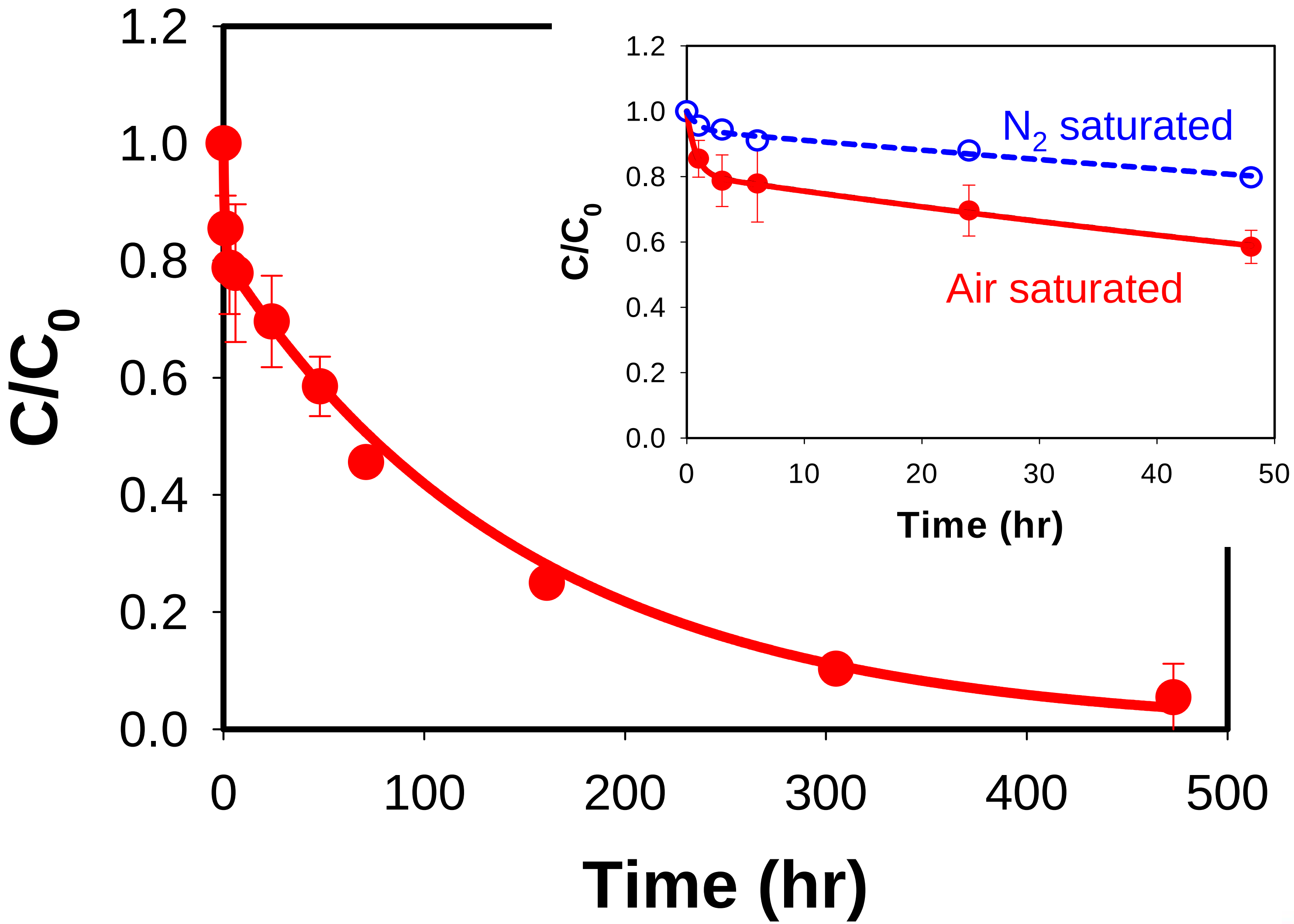


single wall nanotubes (SWNT)

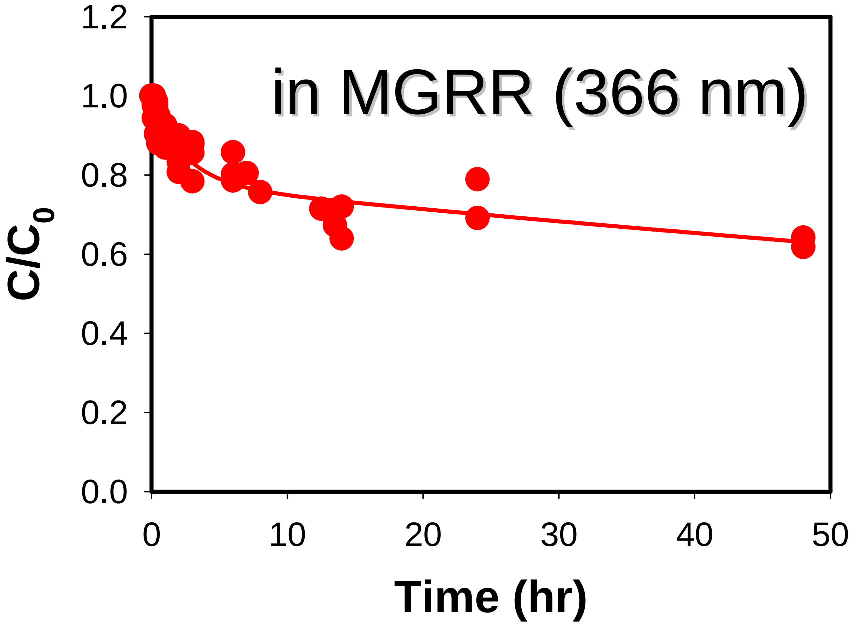


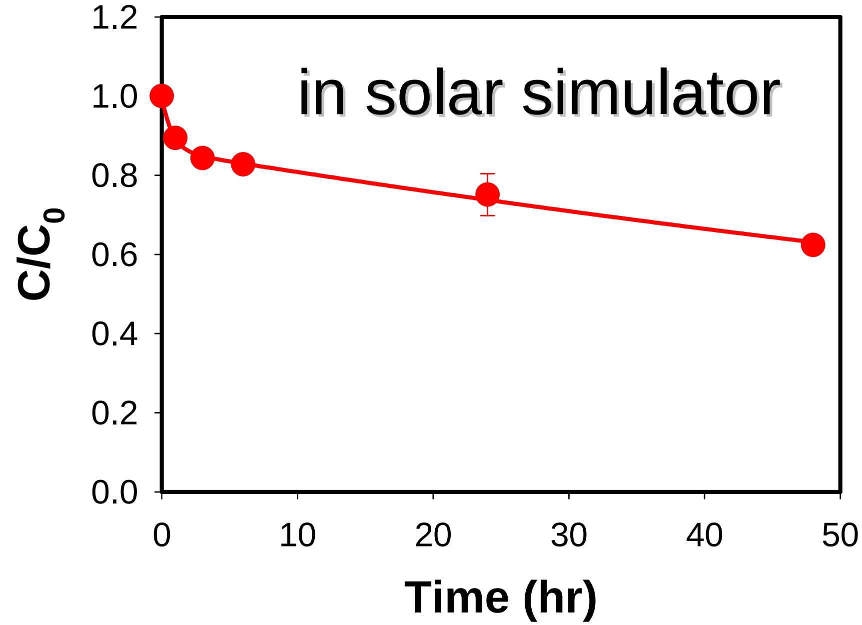
fullerenol isomers

Fullerenol Degradation under Simulated Solar Irradiation



Fullerenol Monochromatic and Solar Irradiation Kinetics (22°C)





$$C = C_0(0.2068e^{-0.3995t} + 0.7793e^{-0.0044t}) \quad C = C_0(0.1376e^{-1.336t} + 0.8627e^{-0.0065t})$$

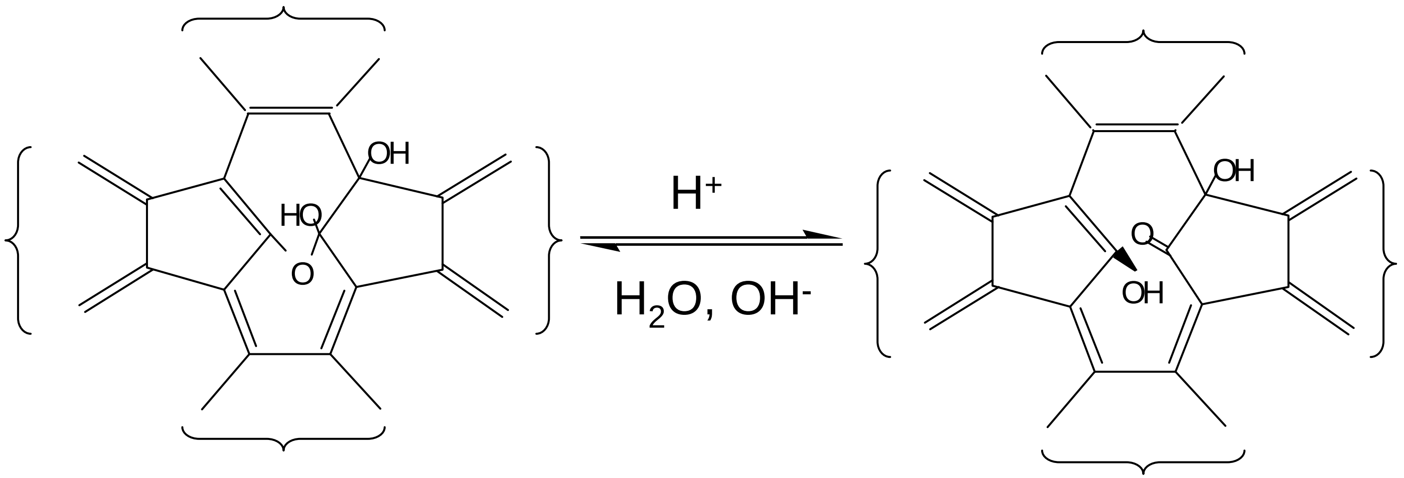
Quantum yield:

fast: 1.55×10^{-3}, slow: 1.71×10^{-5}

pH Dependence of Kinetic Parameters for Direct Photoreaction of Fullerenol

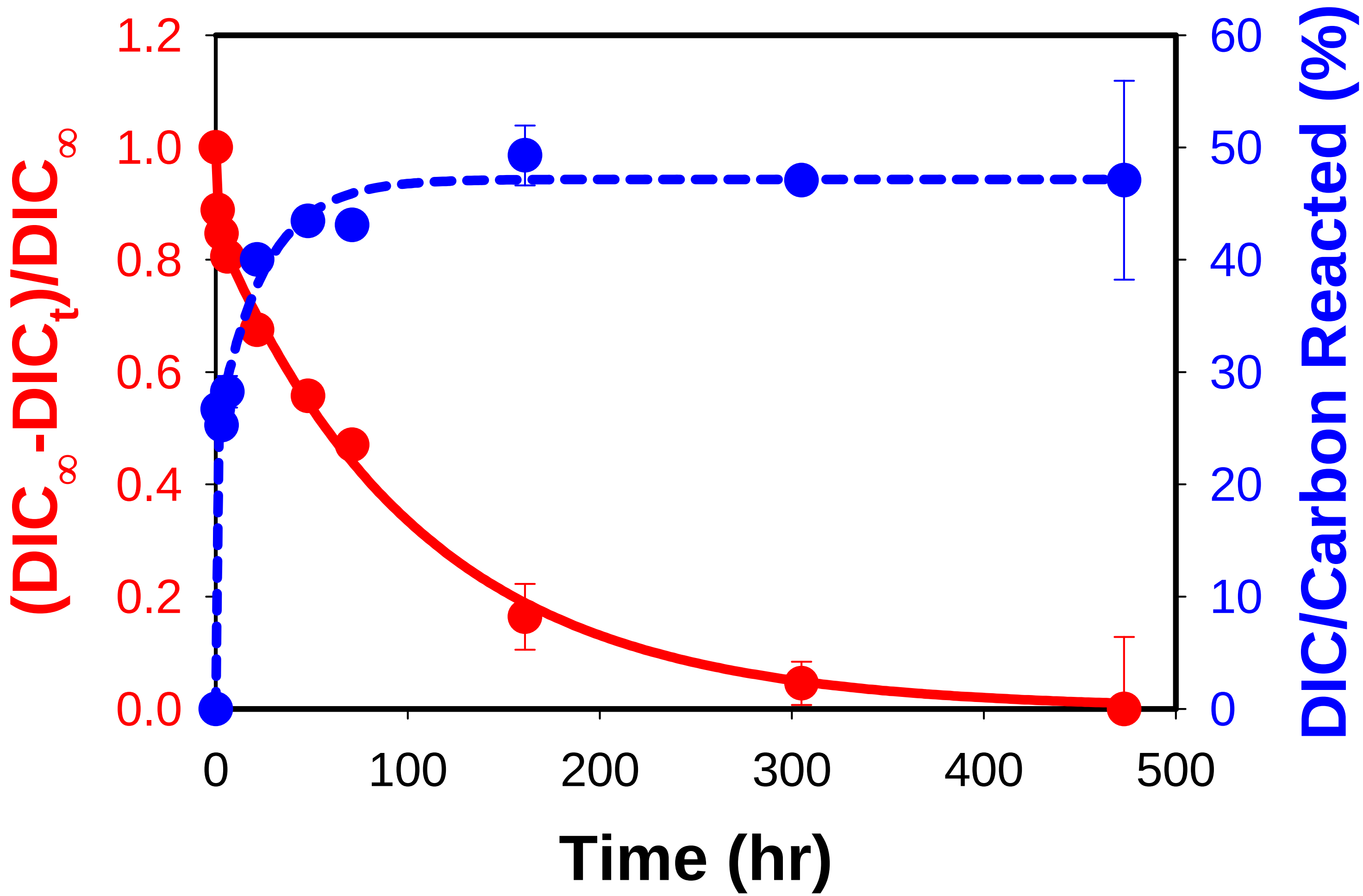
	k_{fast} (hr^{-1}) (±1sd)	f_{fast} (±1sd)	k_{slow} (hr^{-1}) (±1sd)	**f_{slow} (±1sd)**
pH 3.0	1.093 ± 0.310	0.154 ± 0.193	(3.94 ± 0.55) × 10^{-3}	0.844± 0.011
pH 6.6	0.314 ± 0.085	0.212 ± 0.193	(3.20 ± 1.12) × 10^{-3}	0.772± 0.027
pH 10.4	0.027 ± 0.0084	0.466 ± 0.109	(2.70 ± 1.03) × 10^{-3}	0.516 ± 0.109

Fullerenol Constituents Include pH Dependent Hemiketals

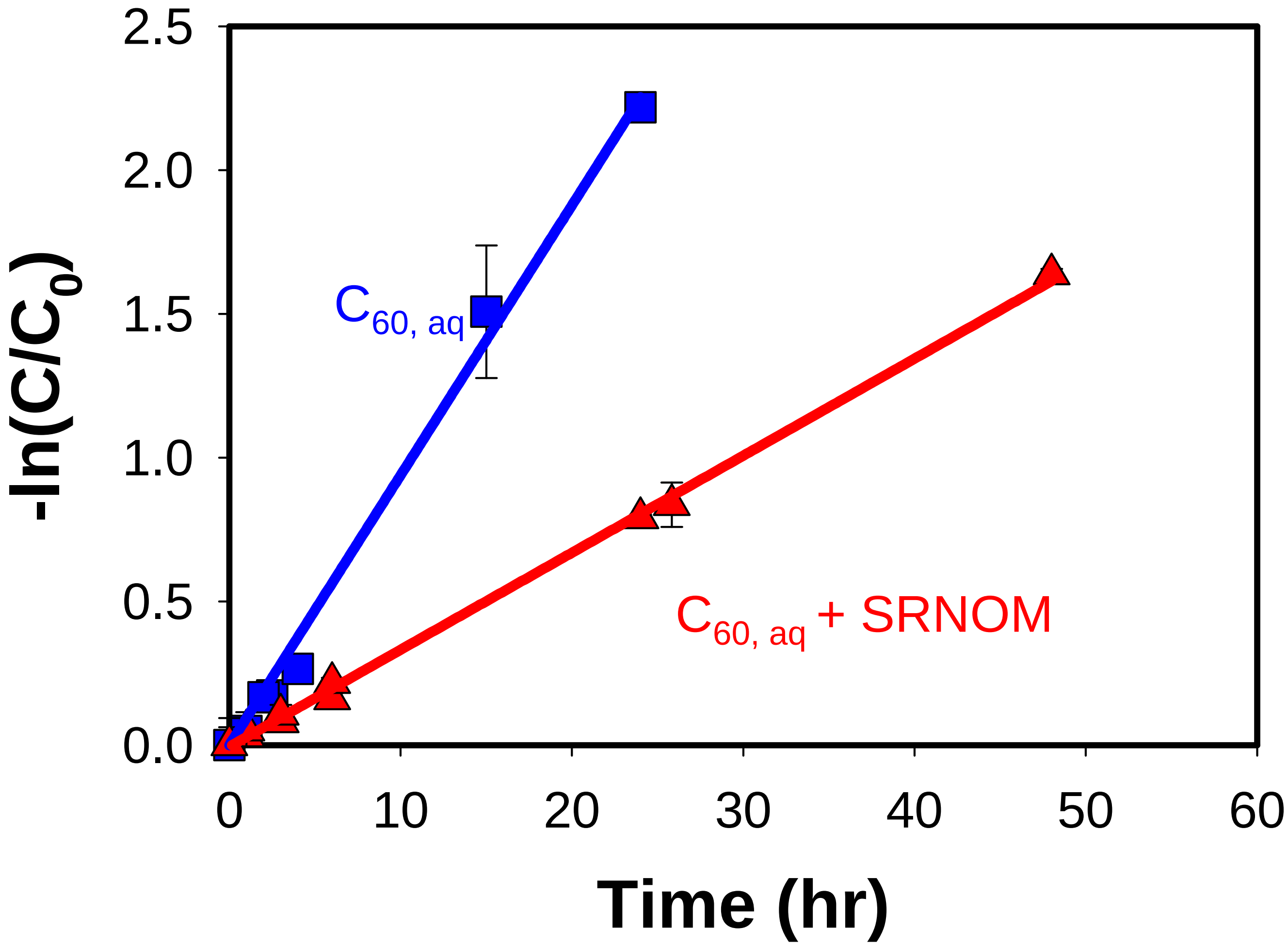


Direct Photomineralization Kinetics of Fullerenol

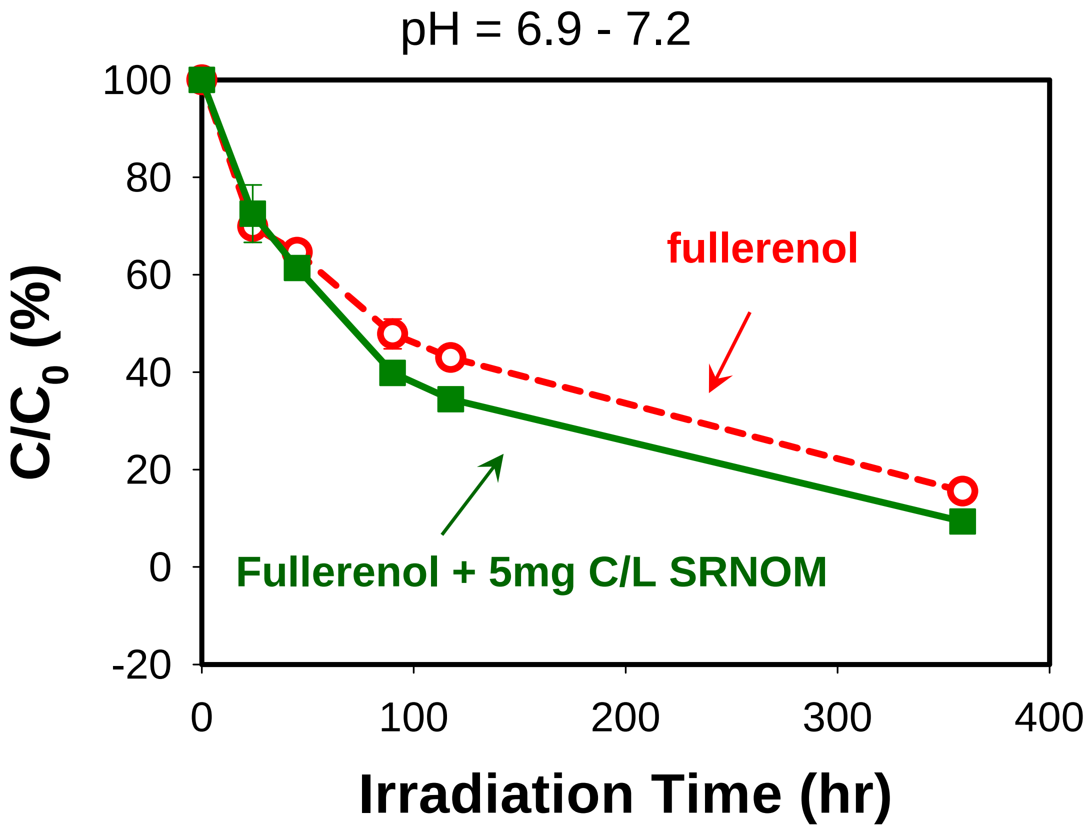
(Simulated Solar Irradiation)



SRNOM Effect on C_{60} Photolysis
Implication: NOM Enhances Dispersion & Persistence



Natural Organic Matter (NOM) Effect on Simulated Solar Irradiation of Fullerenol



DIC photoproduction also is enhanced

Calculation of the Enhancement/ Attenuation Factor

Apparent enhancement factor of NOM, *EF*

$$EF = k_{obsd} / k_{ful}$$

k_{obsd} and k_{ful} is the first order rate constant of fullerenol solution in the presence and absence of SRNOM, respectively.

Light attenuation factor of NOM, *S*

$$S = \frac{1 - \exp(-a_{330} l)}{a_{330} l}$$

Effect of NOM on the Photodegradation of Fullerenol

SRNOM (mg C /L)	k_{obsd} (hr^{-1})	*EF*	a_{330} (m^{-1})	initial *S*	*EF Corr.*
0	0.0074	1.00	0.12	1.00	1.00
2.5	0.0095	1.28	31.16	0.85	1.51
5.0	0.0085	1.15	38.89	0.81	1.42
10.0	0.0057	0.77	55.65	0.75	1.03

Possible Mechanisms for Light-Induced NOM Interaction

- Intramolecular photoreactions of NOM-Full Aggregates –

$$\mathrm{NOM} + \mathrm{FUL} \rightleftarrows \mathrm{NOM{:}FUL} \xrightarrow{h\nu} \mathrm{Products}$$

Site saturation leads to plateau in EF vs [NOM]

- NOM is both source and sink for reactive transients that mediate fullerenol photoreaction

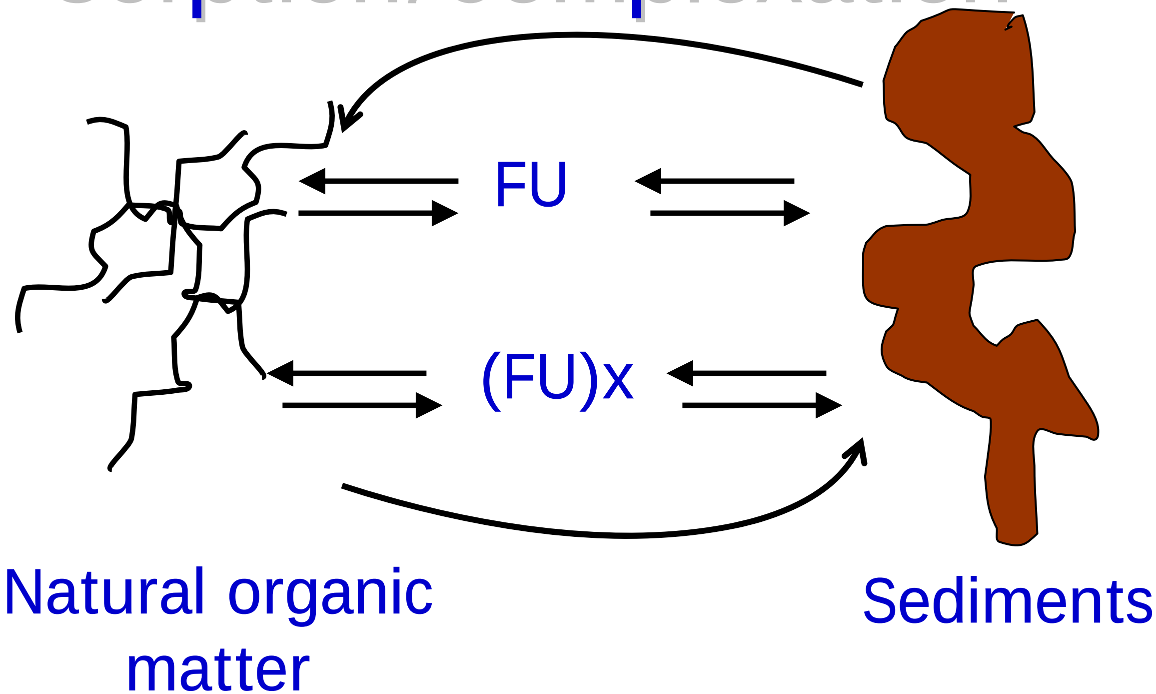
$$\mathrm{NOM} \longrightarrow \mathrm{ROS\ (e.g.\ OH)}$$

$$\mathrm{ROS} \longrightarrow \begin{cases} \xrightarrow{\mathrm{NOM}} \\ \xrightarrow{\mathrm{FUL}} \end{cases}$$

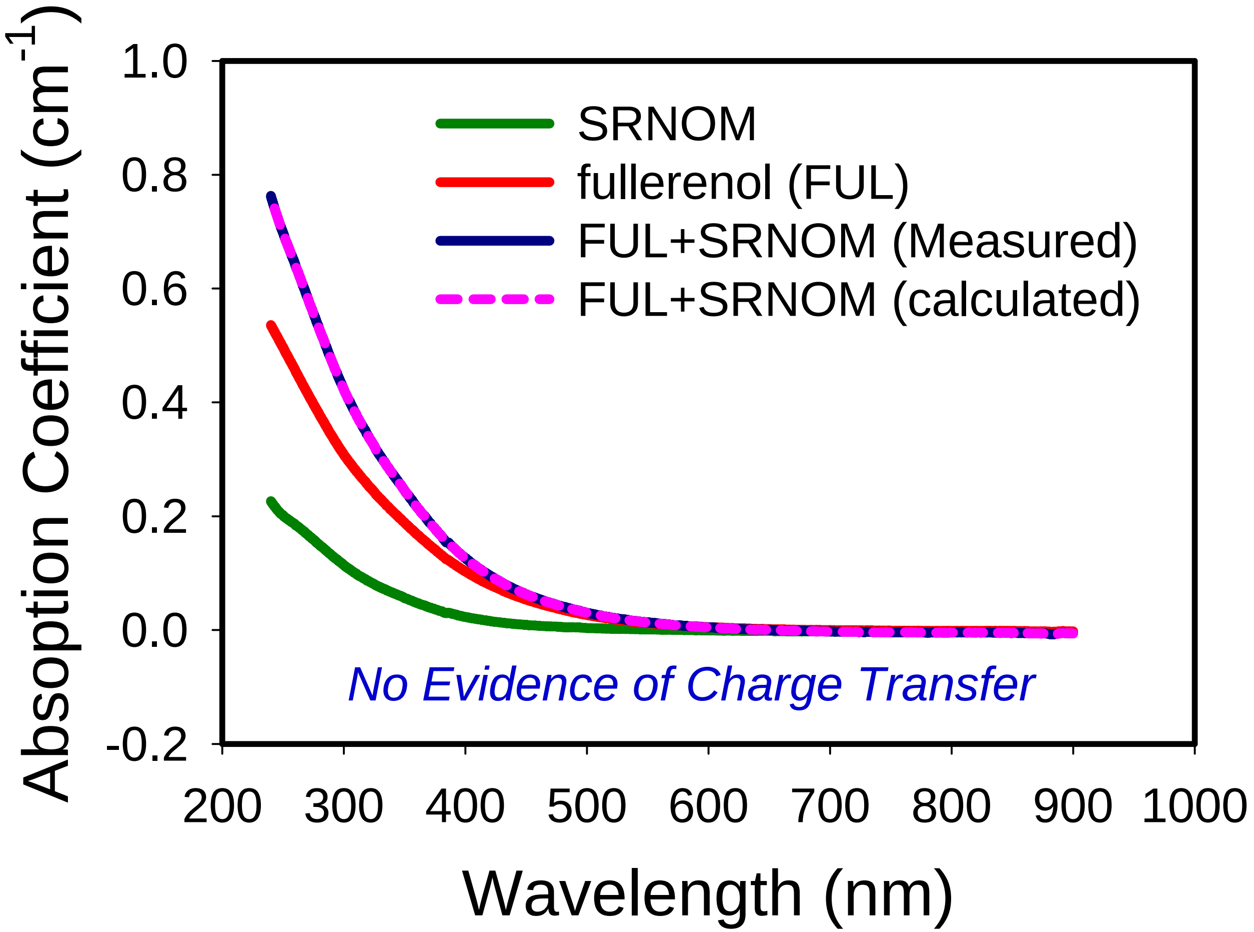
Agglomeration

$$\mathrm{FU} \xrightarrow{x\mathrm{FU}} (\mathrm{FU})x$$

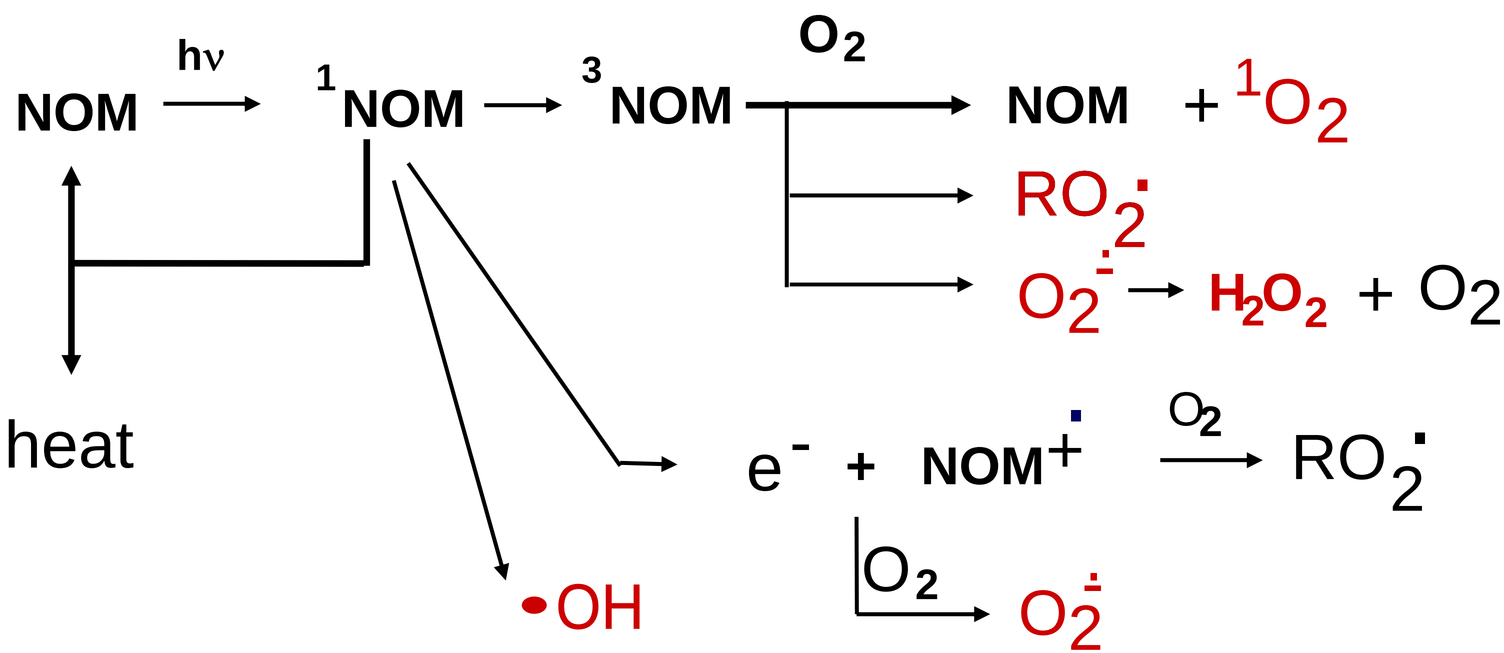
Sorption/Complexation



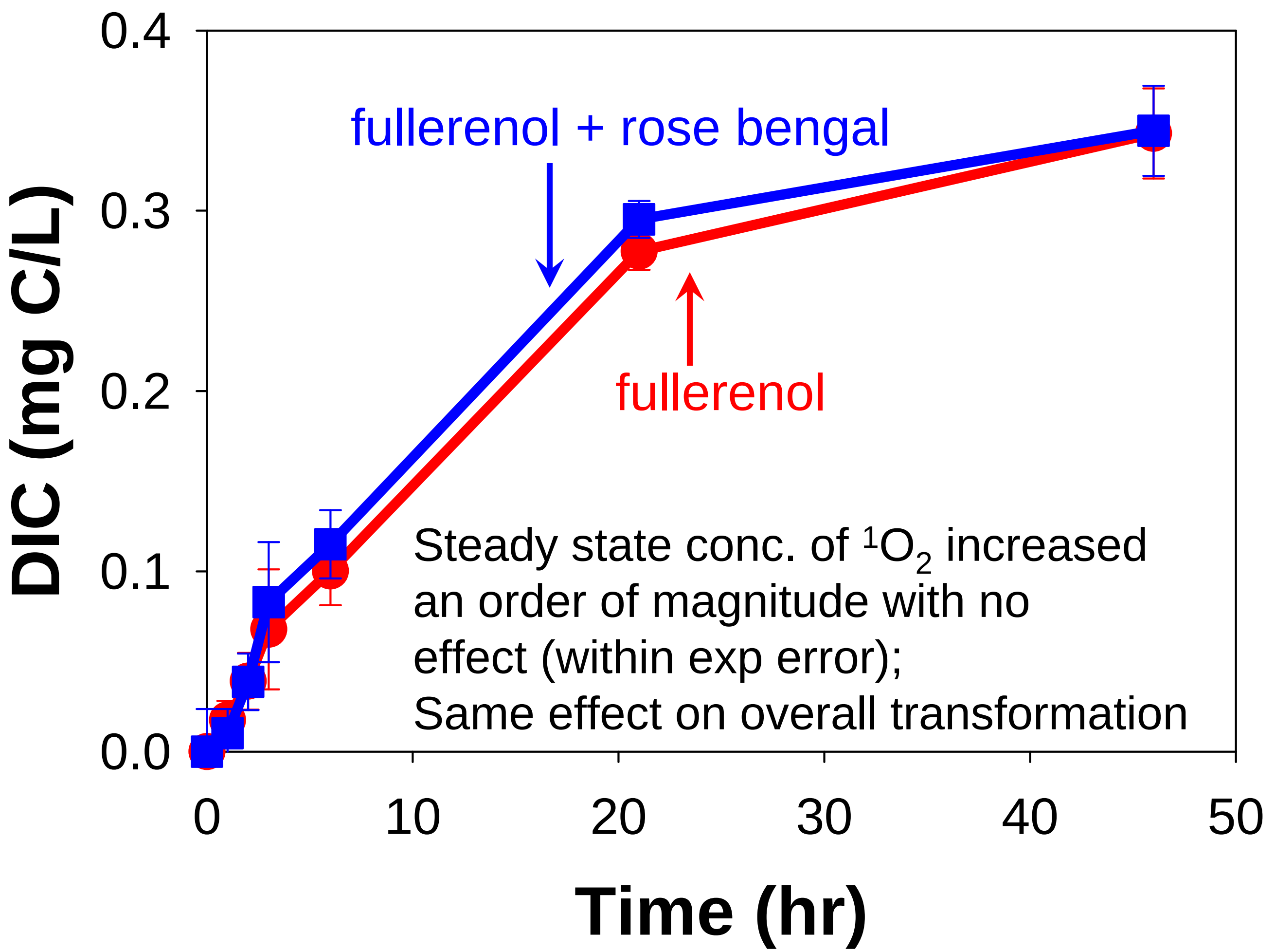
Mixtures of SRNOM and Fullerenol Have Additive Absorption Spectra



Reactive Oxygen Species
Photoproduced From NOM



Rose Bengal Effect on DIC Production by Fullerenol



However, singlet oxygen reaction within NOM/Ful aggregates could be involved

Determination of 2^{nd} Order Rate Constant (k_{ful}) for OH Reaction with Fullerenol

Scavenger, Octanol

$NO_3^- \xrightarrow{hv} OH^{\bullet} \rightarrow$

Fullerenol

First-Order Method

k_{ful} [FUL] << k_{oct}[OCT]

-predominant reaction of OH is with octanol scavenger

Kinetic equations:

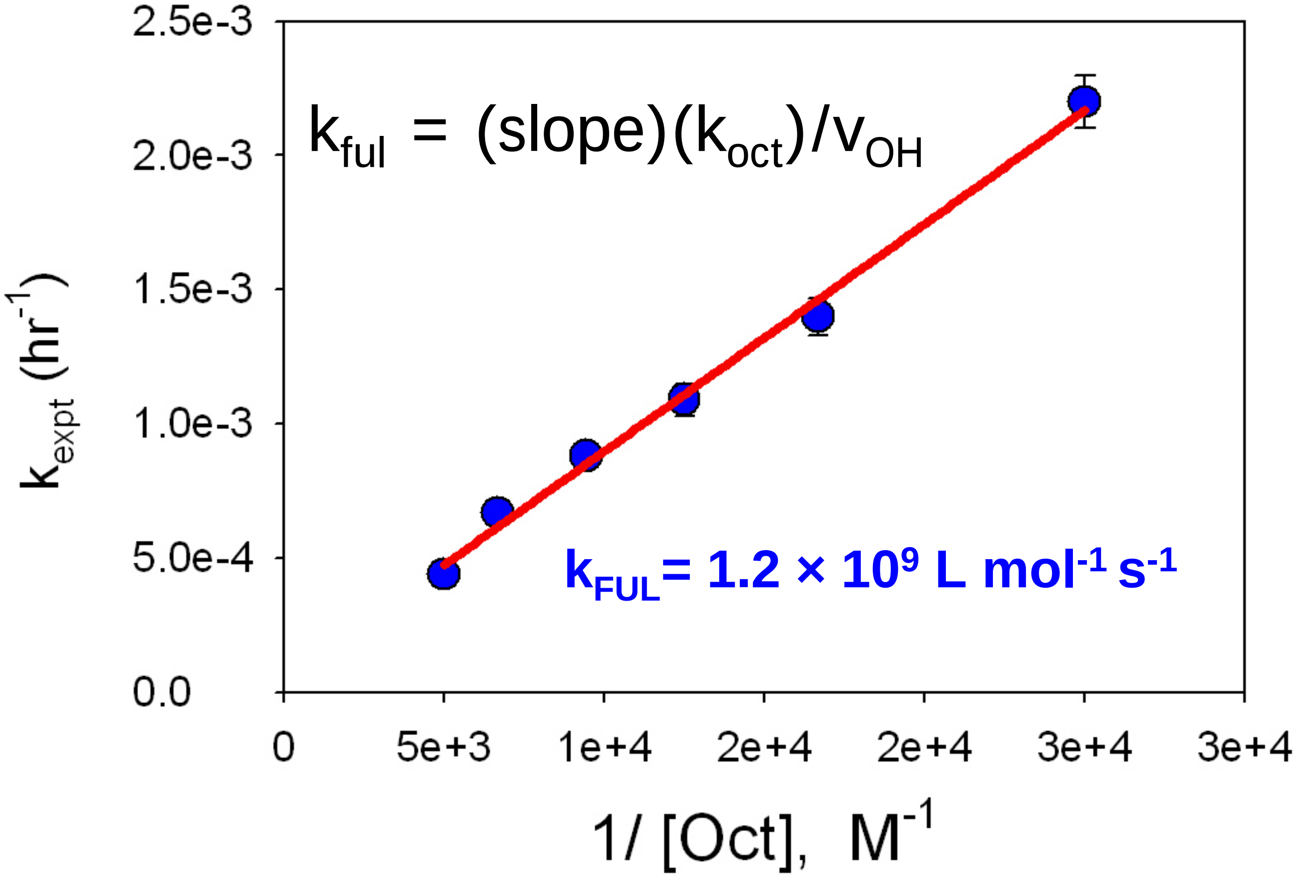
$$v_{OH} = k_{a,\lambda}\phi_{OH}[NO_3]$$

$$k_{\exp t} = \frac{v_{OH}\ k_{ful}}{k_{oct}[OCT]}$$

Slope of k_{expt} vs 1/[OCT] used to compute k_{ful}

* Zepp et al. 1987, Environ. Sci. Technol., **21**, 443-450

Fullerenol Reaction With OH Radical Nitrate/Octanol System at 313 nm



Conclusions

- Fullerenol photoreaction is enhanced in presence of NOM; C_{60} photolysis is retarded
- Photomineralization is a primary pathway for direct and NOM-enhanced photoreaction
- Dependence of enhancement on NOM concentration suggests either site saturation involving NOM-fullerenol aggregates or NOM scavenging of NOM-produced ROS
- Reaction via singlet oxygen in bulk water not likely but intramolecular pathway in aggregates possible.
- OH radicals react with fullerenol rapidly ($k = 1.2 \times 10^9$ M-1 s^{-1}) so NOM may degrade fullerenol via OH mediated path.

Acknowledgements

- Chad Jafvert
- Dermont Bouchard
- Jim Weaver
- Eric Weber
- Cissy Ma