Investigation of Mechanisms of Light-Initiated Interaction between Fullerenes and Natural Organic Matter

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Outline

- Background
- Research objectives
- Results and discussion
- Summary
- Acknowledgements

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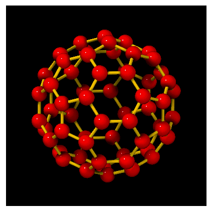
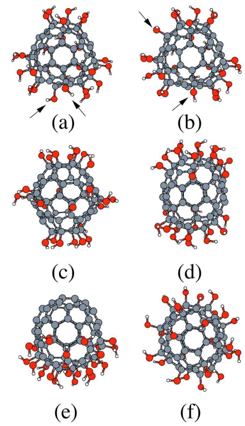
Fullerene and Derivatives

- For the past decade, the chemical and physical properties of fullerene have been a hot topic in the field of research and development, and are likely to continue to be for a long time
- Fullerenes are stable, but not totally unreactive



C_{60}



Fullerenol isomers

Guirado-López and Rincón, 2006

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Natural Organic Matter (NOM)

- NOM is a collective term, assigned to the realm of all of the degraded organic materials from plants and animals in the environment.
- NOM is present throughout the environment.
- NOM can act as the source and sink of many reactive transients.
- NOM is regarded as supramolecular assemblies, which can provide a microenvironment differing from the bulk aqueous phase.

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Research Objectives

- Effect of NOM on the photoreaction kinetics of C_{60} and fullerenol
- Investigation of the function of reactive oxygen species (ROS), i.e. singlet oxygen, superoxide and hydroxyl radicals, on the photoreaction of C_{60} and fullerenol
- Propose mechanisms of NOM effect on the photochemistry of C_{60} and fullerenol

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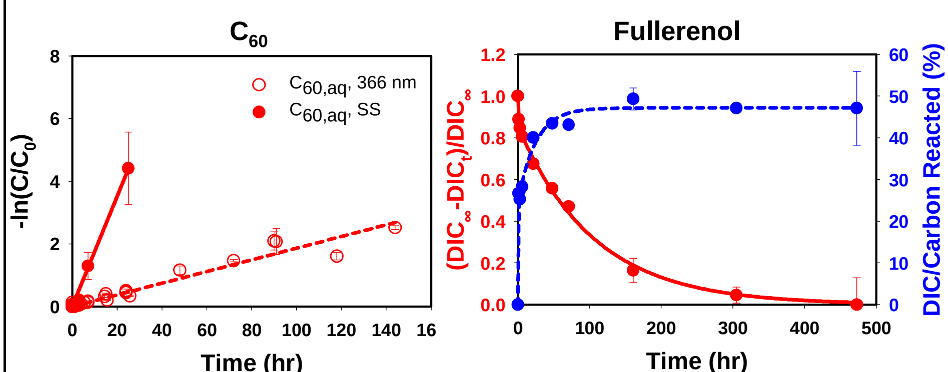
Photoreaction Kinetics of C_{60} and Fullerenol



linear kinetics

Biexponential kinetics

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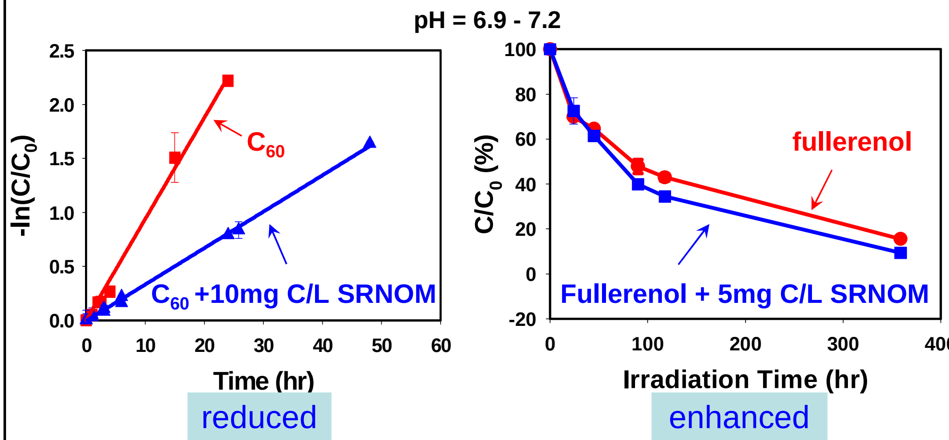
Effect of NOM on the Photoreaction of C_{60} and Fullerenol



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Attenuation/Enhancement Factor of NOM

- Apparent enhancement/attenuation factor of NOM, S_{app}

$$S_{app} = k_{obsd} / k_{Fu}$$

k_{obsd} and k_{Fu} is the first order rate constant of C_{60} suspension or fullerenol solution in the presence and absence of SRNOM, respectively.

- Light attenuation factor of NOM, *SF*

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

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Effect of NOM on the Photodegradation of C_{60} and Fullerenol

	SRNOM (mg C /L)	k_{obsd} (hr^{-1})	S_{app}	initial *SF*	S_{corr}
C_{60}	10	0.0356	0.34	0.75	**0.45**
fullerenol	5	0.0085	1.15	0.81	**1.42**
	10	0.0057	0.77	0.75	**1.03**

$a_{330} = 55.65\ m^{-1}$

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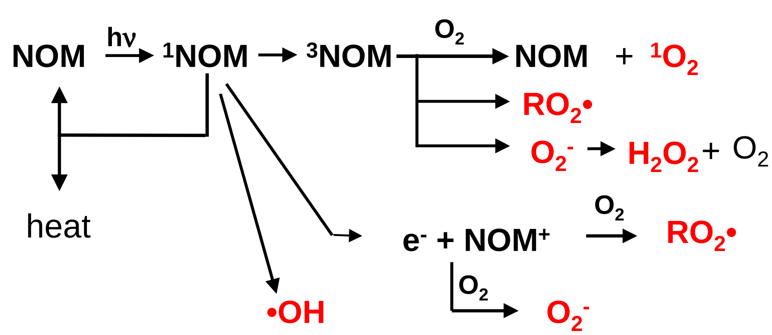
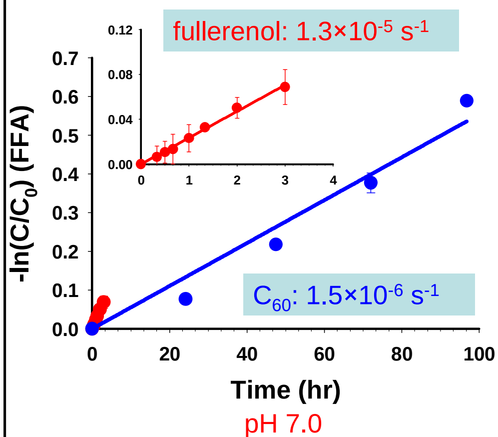
Photoproduction of Reactive Oxygen Species (ROS) from NOM



Production of Singlet Oxygen by C_{60} and Fullerenol



$$\frac{d[FFA]}{dt} = k_r [^1O_2]_{ss} [FFA]$$

$$\frac{d[FFA]}{dt} = k_{obs} [FFA]$$

$$[^1O_2]_{ss} = \frac{k_{obs}}{k_r}$$

$$k_r = 1.2 \times 10^8 M^{-1} s^{-1}$$

rate constant for reaction with $^1O_2$ in surface water:

Fullerenol: 10^{-5}-10^{-2} hr^{-1}

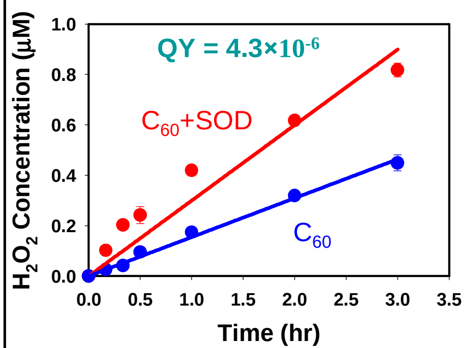
C_{60}: 10^{-6}-10^{-3} hr^{-1}

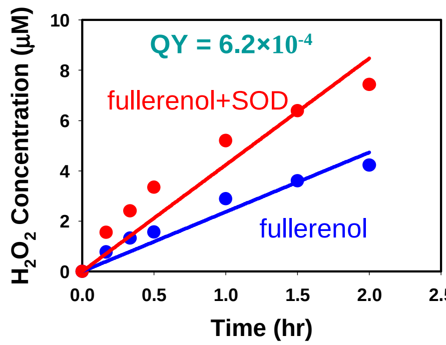
Consumption of Singlet Oxygen by C_{60} and Fullerenol

- When C_{60} or fullerenol **mixed with Rose Bengal** under exposure of monochromatic light at 366 nm, no increase of photoreaction rate was observed.
- When C_{60} and fullerenol were mixed with **singlet oxygen generated thermally**, and reacted in dark, no observable change of photoreaction rate was found.

Singlet oxygen in bulk solution is not likely a significant factor during the photoreaction of C_{60} and fullerenol.

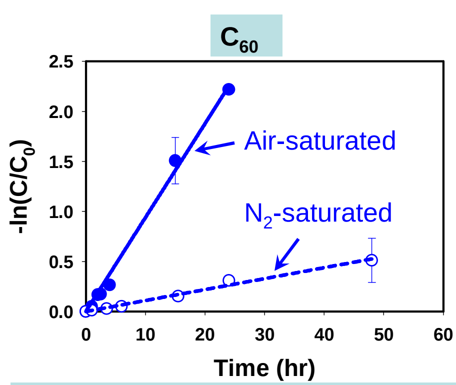
Superoxide Production of C_{60} and Fullerenol

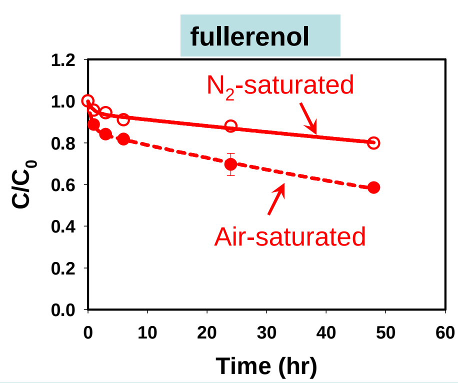




O_2^-/HO_2 are byproducts of the photoreaction of C_{60} and fullerenol, the production rate was increased on the addition of SOD.

Oxygen Effect on the Photoreaction Kinetics of C_{60} and Fullerenol





The photoreaction of **C_{60}** was slowed by about a factor of **9**, while that of **fullerenol** was slowed by about a factor of **2** in N_2-saturated compared to air-saturated solution.

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Estimation of •OH *

NO_3^- —light→ •OH → C_{60} or fullerenol
•OH → scavenger (1-octanol)

$$k_{a,\lambda} = 2.303 I_{\lambda} \varepsilon_{\lambda} l$$

$$v(\lambda) = k_{a,\lambda} \phi_{OH} [NO_3]$$

$$\frac{k_M}{k_{\text{expt}}} = \frac{1}{[\cdot OH]_{ss}} = \frac{k_w}{\upsilon} + \frac{k_{oct}[OCT]}{\upsilon}$$

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

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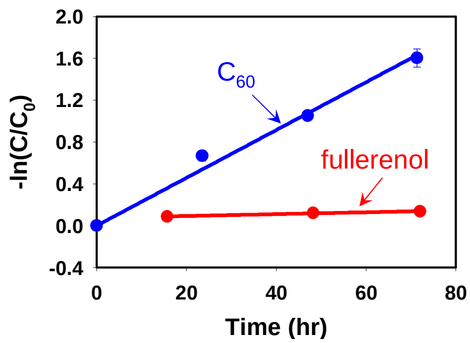
Consumption of Hydroxyl Radicals by C_{60} and Fullerenol



in the presence of $NaNO_3$ and 1-octanol

	k **(L mol^{-1} s^{-1})**	**$[\cdot OH]_{ss}$** **(mol L^{-1})**
Fullerenol	1.2E9	2.0E-16
C_{60}	5.4E9	1.2E-15

k = 2nd order rate constant
$[\cdot OH]_{ss}$= steady state •OH concentration

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Possible Mechanisms for Light-Induced NOM-Fullerene Interaction

- Intramolecular photoreactions of NOM-FU Aggregates

$$\text{NOM} + \text{FU} \rightleftharpoons \text{NOM:FU} \xrightarrow{h\nu} \text{Products}$$

FU represents fullerene or fullerene derivatives

- NOM is both source and sink for reactive transients that mediate C_{60} and fullerenol photoreaction

$$\text{NOM, FU} \longrightarrow \text{ROS (e.g. } ^1O_2,\ O^{2-}/HO_2,\ \bullet OH)$$

$$\text{ROS} \longrightarrow \text{NOM}$$

$$\text{ROS} \longrightarrow C_{60}\text{, fullerenol}$$

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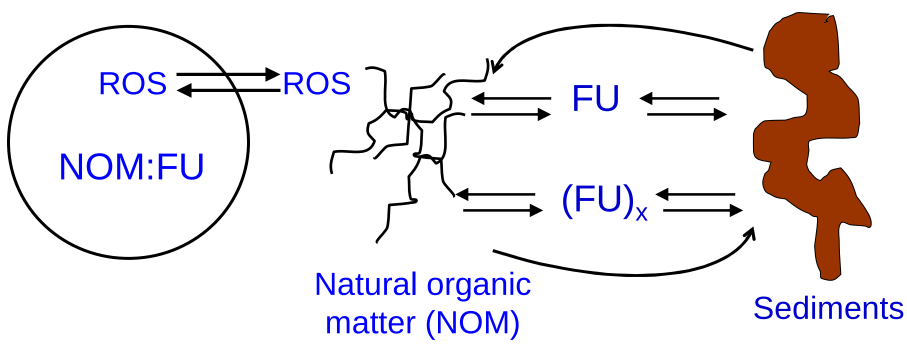
Agglomeration

$$\text{FU} \xrightarrow{x\text{FU}} (\text{FU})_x$$

Cage Formation

Sorption/Complexation



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Conclusions

- NOM **reduced** the photoreaction rate of C_{60}, however **enhanced** the photodegradation of fullerenol
- Both C_{60} and fullerenol can generate singlet oxygen ($^1O_2$) and superoxide/hydroperoxyl radicals (O^{2-}/HO_2) under irradiation. No singlet oxygen consumption was observed during the irradiation of C_{60} and fullerenol
  - photoreaction via $^1O_2$ and O^{2-} in the bulk water are not likely a major pathway
  - an intramolecular pathway involving aggregates is possible

Conclusions (cont'd)

- Fullerenol and C_{60} react with hydroxyl radicals (•OH) rapidly with rates of 1.2×10^9 and 5.4×10^9 L mol^{-1} s^{-1}, respectively
  - NOM may mediate fullerenol and C_{60} photoreaction via OH radicals
- NOM can act as both scavenger and generator of ROS, the balance between scavenging and generation of ROS may be altered because of microheterogeneous formation and reactions of the transients in fullerene or fullerene-NOM clusters

Acknowledgements

- National Research Council (NRC)

Questions?

Comments?