Current Perspectives on Ozone Chemistry in Marine Life Support Systems

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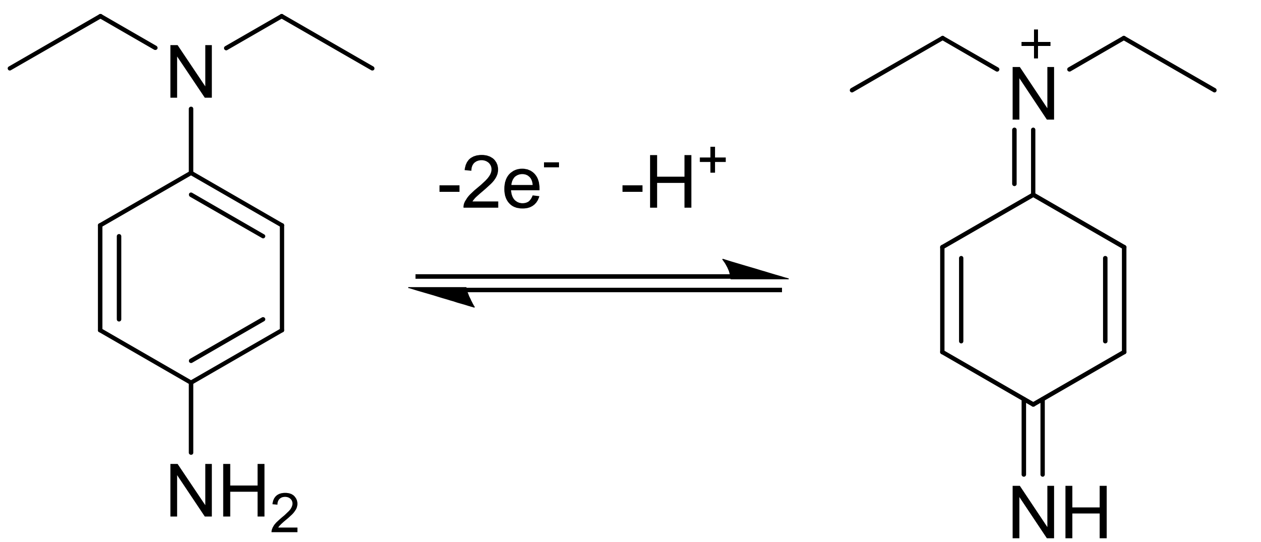
Outline

- Total Residual Oxidants – Measurement
- ORP Theory and Practice
- Primary Ozone Disinfection – Organic
- Secondary DBP Formation – Inorganic
- Acid – Base Chemistry of HOBr
- Ozonation Studies
- Ozone Kinetics Model
- Ozone Reactor Design Model
- Foam Fractionator Design Model
- Future Work

TRO (Total Residual Oxidants)

- Iodometric Titration
- *N*,*N*-diethyl-*p*-phenylenediamine
- ORP (Oxidation Reduction Potential)



DPD

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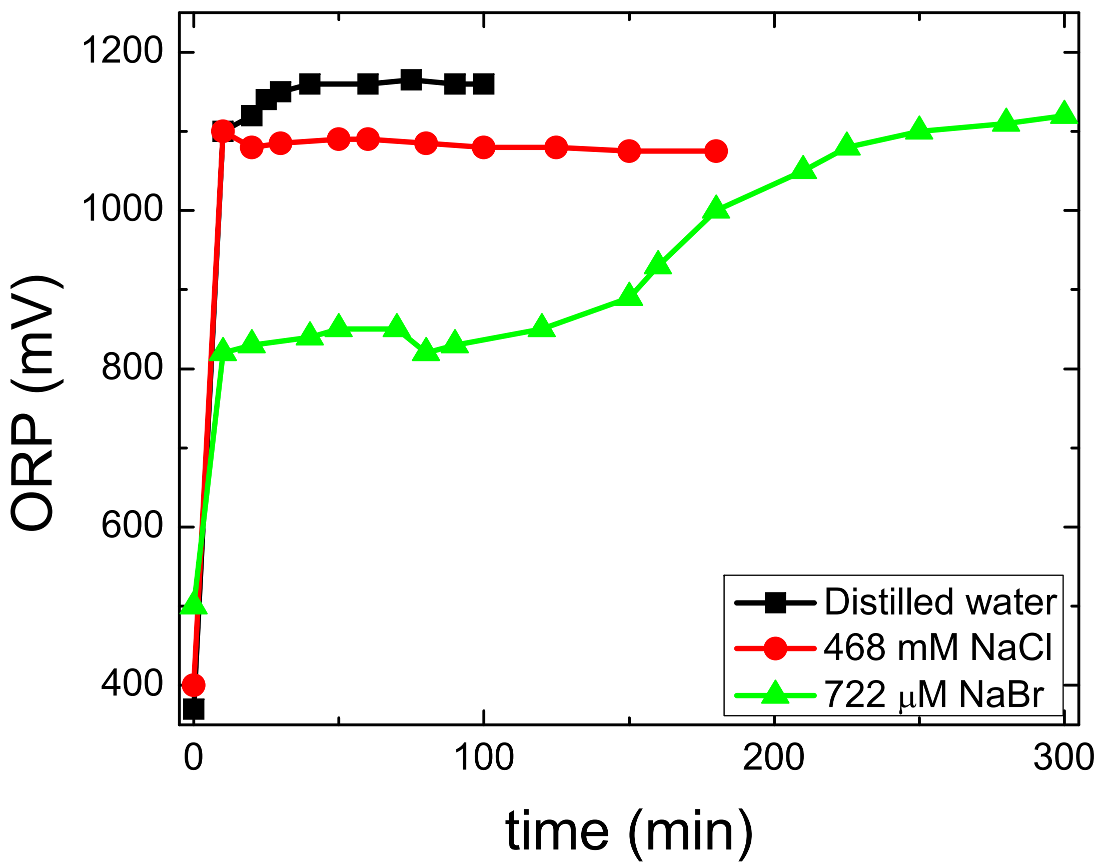
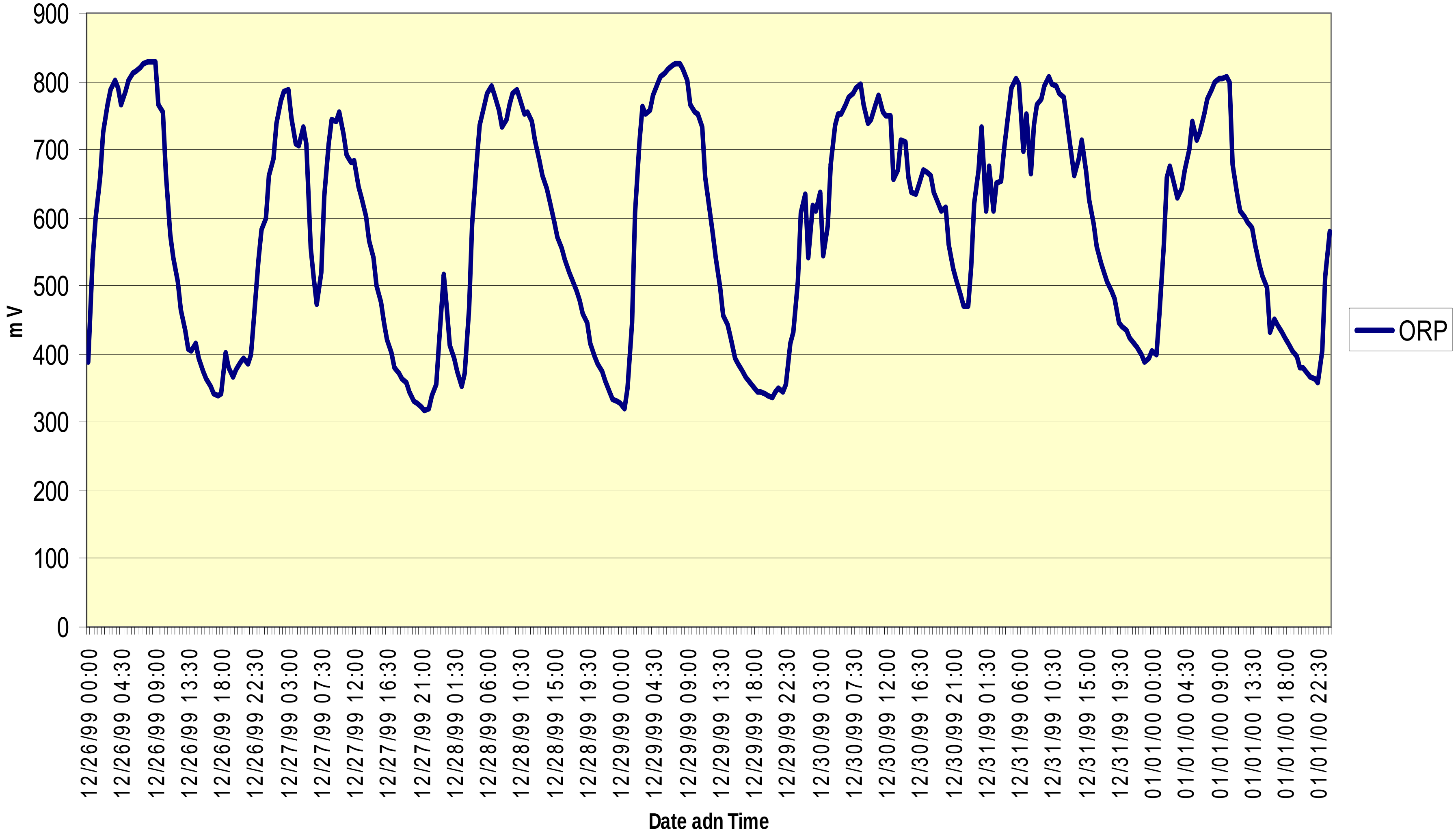
ORP Regimes

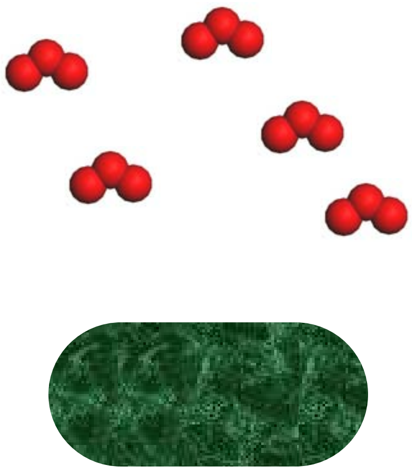
1000-1200 mV	Ozone
700-900 mV	HOX
400-600 mV	Nitrate, Oxygen
0-200 mV	Nitrite
-200-0 mV	Sulfide

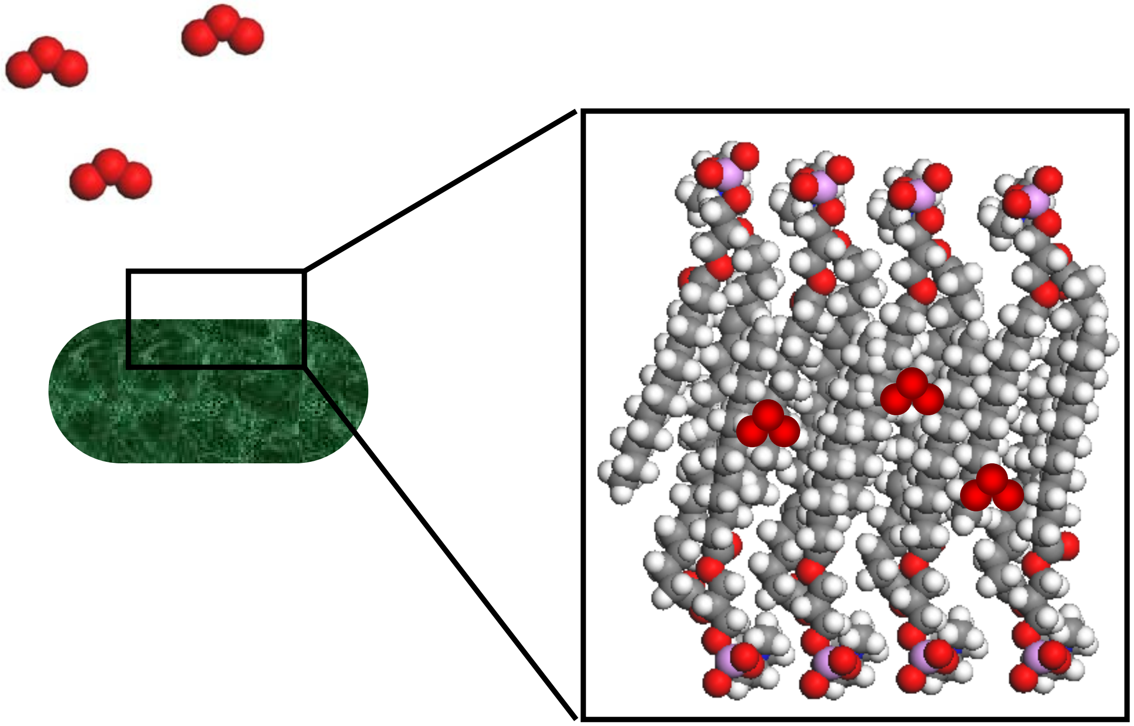


ORP (mV)
1200
1000
800
600
400
0
100
200
300
time (min)
Distilled water
468 mM NaCl
722 μM NaBr

Otter System







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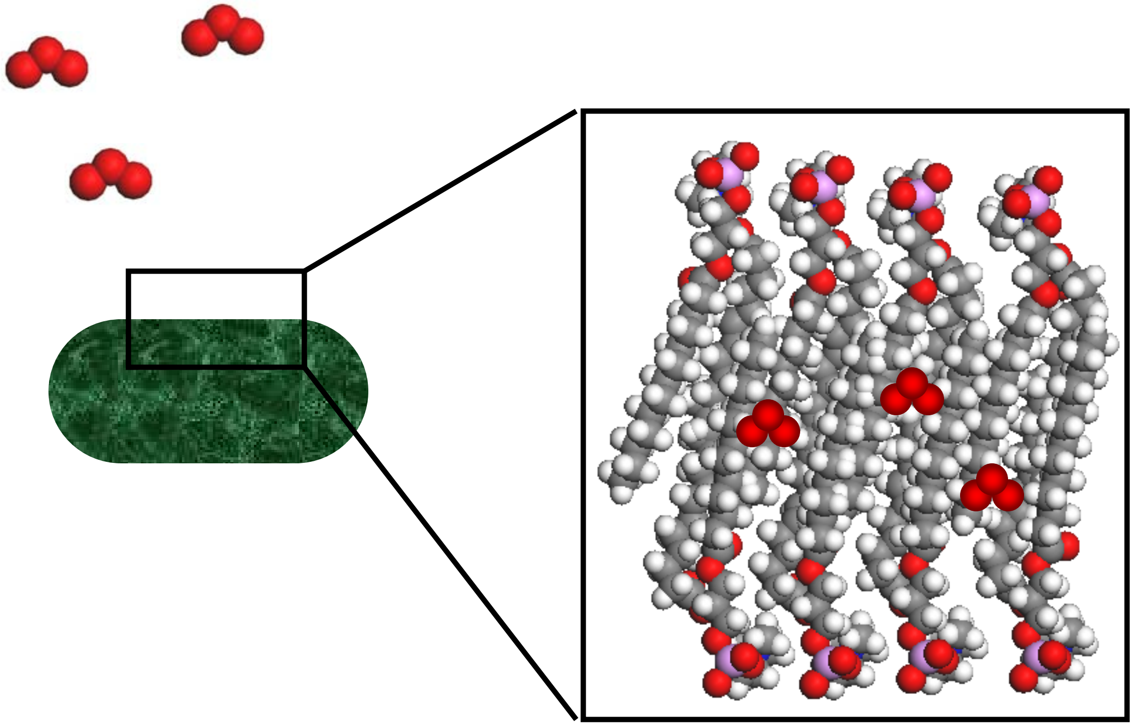

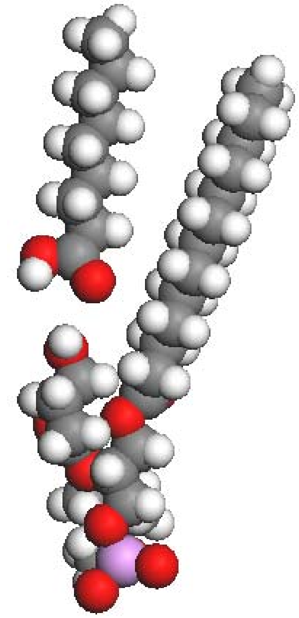

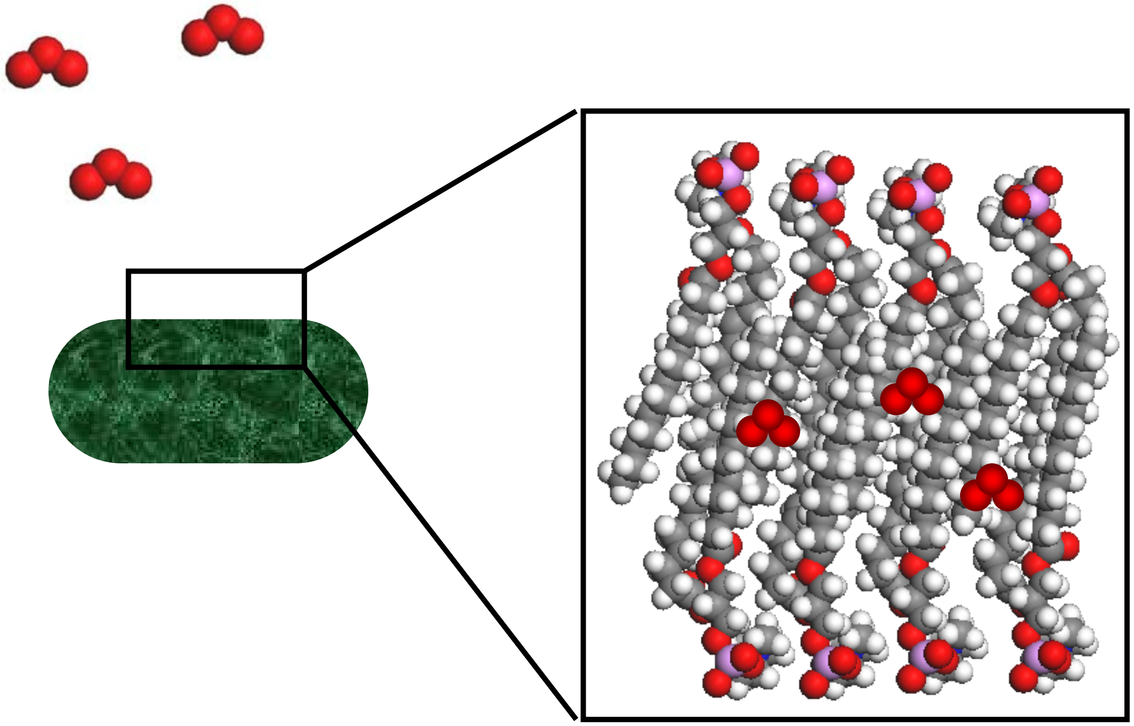

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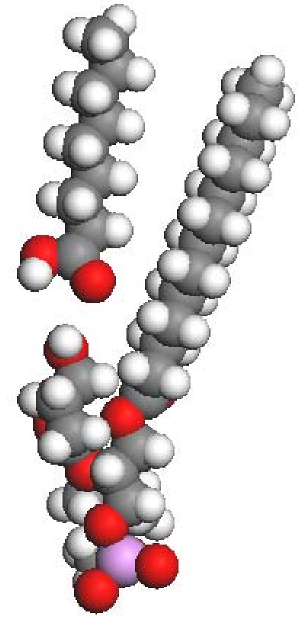

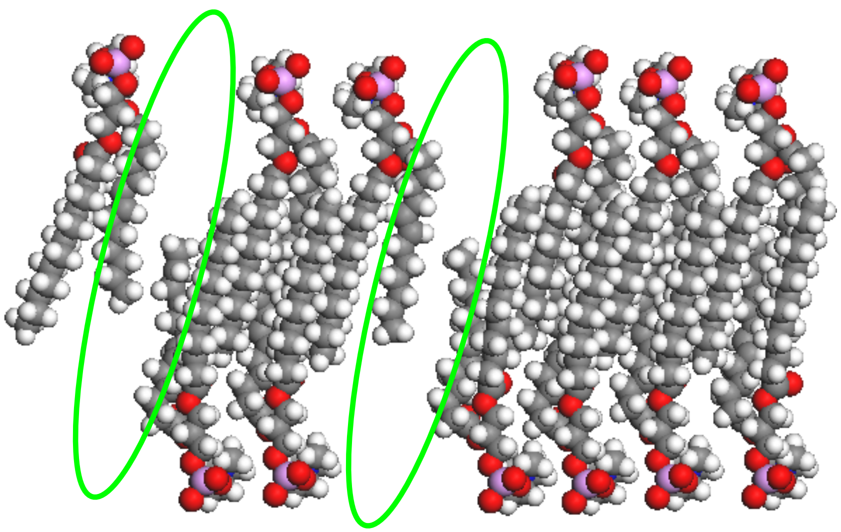

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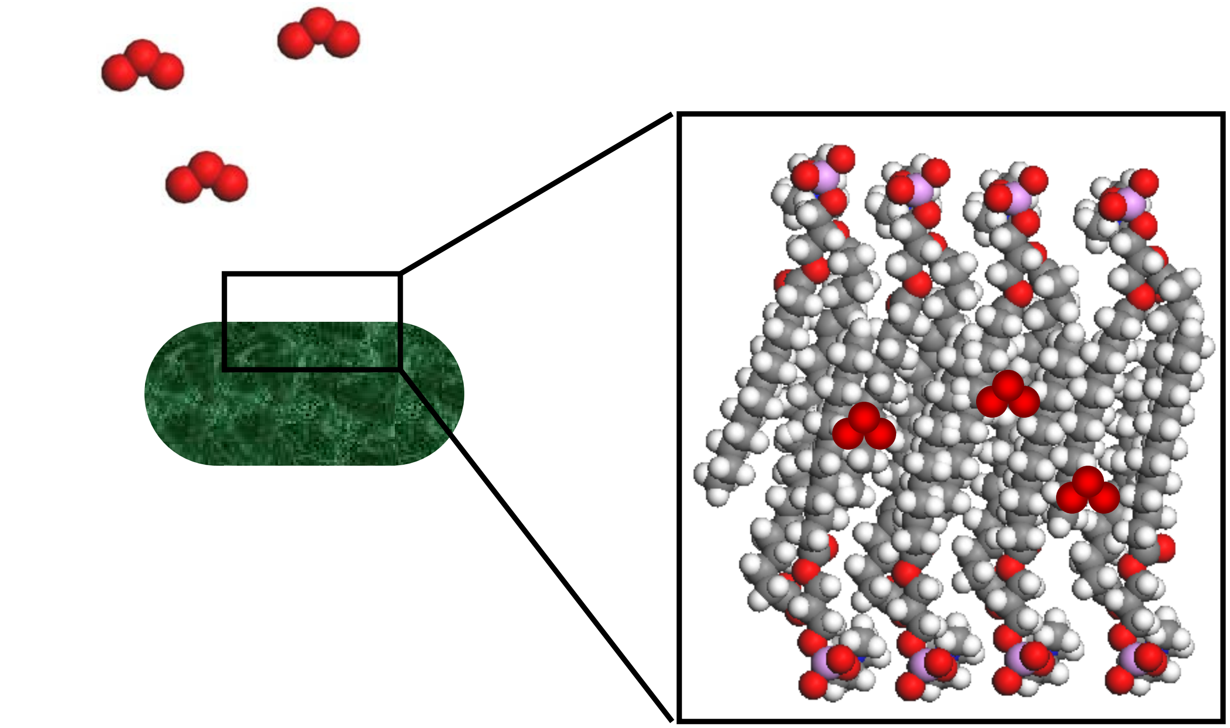
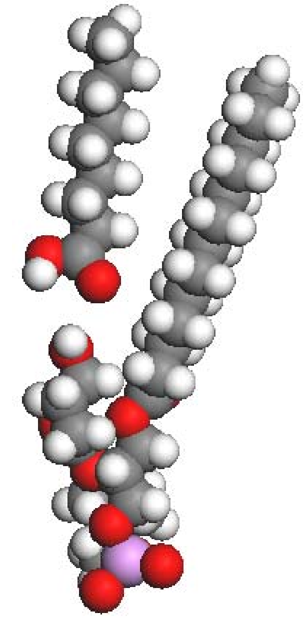
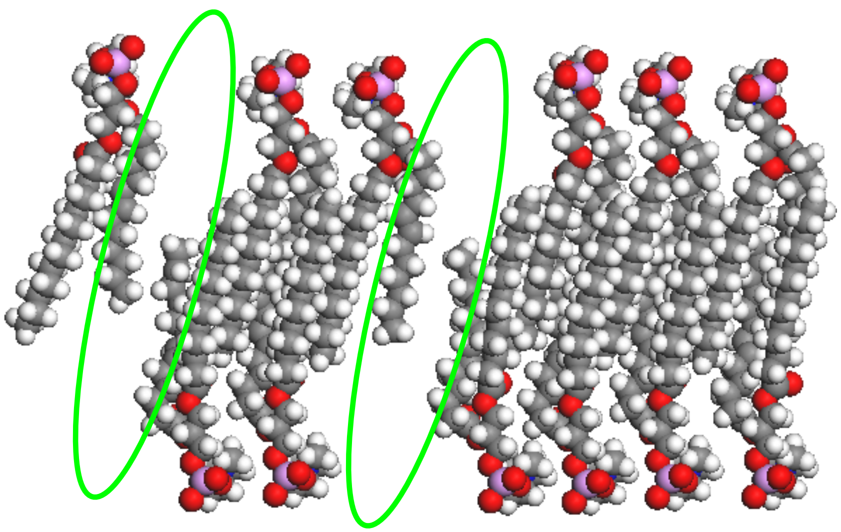
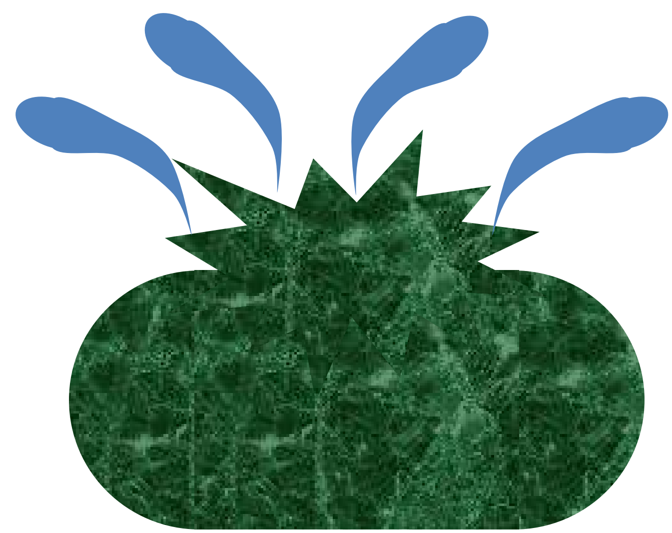
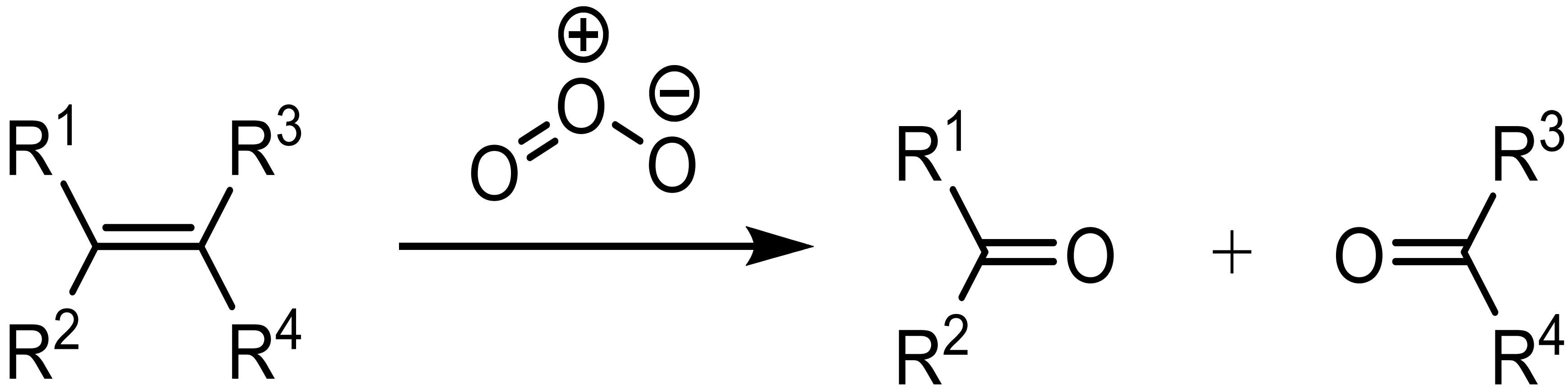
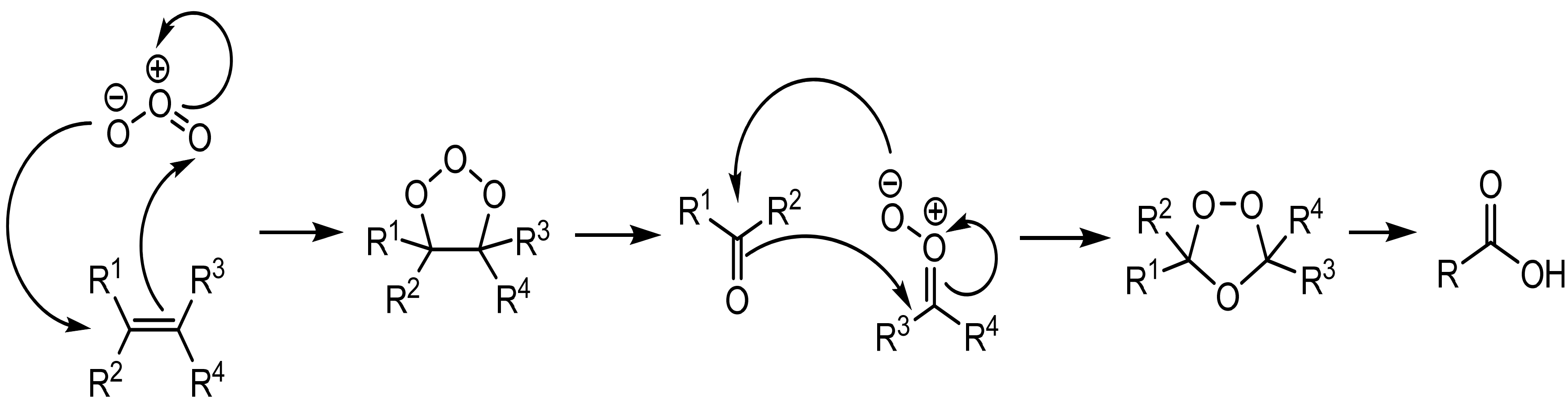












O
O
O
R1
R3
R2
R4
R1
R2
R3
R4
O
R1
R2
O
O
O
R3
R4
R2
O−O
R4
R1
O
R3
O
R
OH

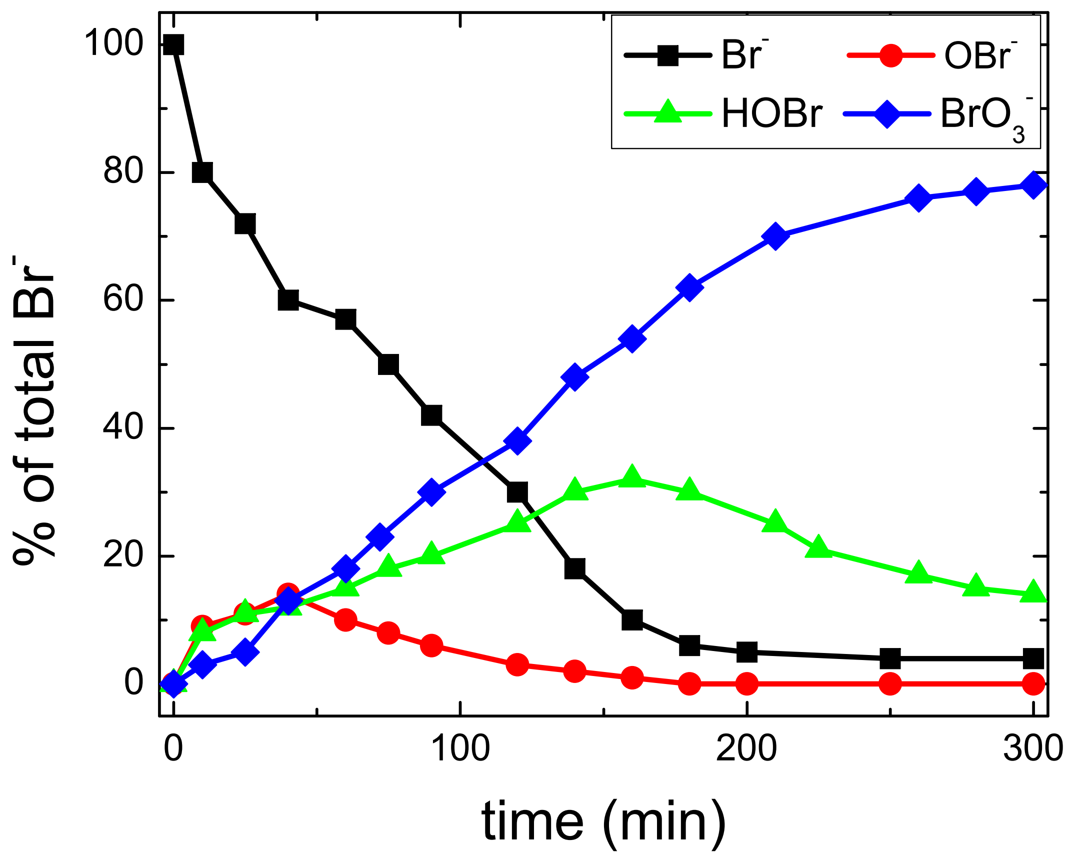
$$O_3(aq) + Br^-(aq) \xrightarrow{k_1} O_2(aq) + BrO^-(aq)$$

$$O_3(aq) + BrO^-(aq) \xrightarrow{k_2} 2O_2(aq) + Br^-(aq)$$

$$2O_3(aq) + BrO^-(aq) \xrightarrow{k_3} 2O_2(aq) + BrO_3^-(aq)$$

$$pH = pKa + \log \frac{[BrO^-]}{[HOBr]}$$

$$Ka = \frac{[H_3O^+][BrO^-]}{[HOBr]} \quad \text{and } pKa = -\log Ka$$



Br-
OBr-
HOBr
BrO3-
100
80
60
40
20
0
% of total Br-
0
100
200
300
time (min)

$$O_3(aq) + Cl^-(aq) \xrightarrow{\text{slow}} O_2(aq) + ClO^-(aq)$$

$$ClO^-(aq) + Br^-(aq) \xrightarrow{\text{fast}} BrO^-(aq) + Cl^-(aq)$$

$$O_3(aq) + Br^-(aq) \xrightarrow{Cl^-} O_2(aq) + BrO^-(aq)$$

$$-\frac{d[O_3]}{dt} = k_1[Br^-][O_3] + (k_2 + 2k_3)[BrO^-][O_3]$$

$$\frac{d[HOBr]}{dt} = k_1[Br^-][O_3] - (k_2 + k_3)[BrO^-][O_3]$$

$$\frac{d[BrO_3^-]}{dt} = k_3[BrO^-][O_3]$$

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Two-minute Ozonation Studies

Table 1. Observed and predicted concentrations of ozone and bromine species at 2.0 min after addition of pure NaBr to ozonated distilled-deionized water.

			Concentration after 2.0 min (uM)		
Solution	$[O_3]$init (uM)	$[O_3]$	[BrOH]total	$[BrO_3^-]$	$[Br^-]$
722 uM NaBr, obs	194	<10	120	<2	602
722 uM NaBr, model	194	0	136	6	580
144 uM NaBr, obs	241	<10	80	13	51
144 uM NaBr, model	241	25	83	14	47

Ozone Kinetics Model Results

Table 2. A model for concentrations of ozone and ozone byproducts after a reaction time of 2.1 min.

Model	$[O_3]$ (uM)	$[BrOH]_{total}$ (uM)	$[BrO_3^-]$ (nM)	$[ClOH]_{total}$ (uM)	[Ox. Organic] (uM)
Initial	0.766	0.00	0.00	0.000	0.000
1	0.238	0.52	0.25	——	——
2	0.231	0.51	0.25	——	——
3	0.197	0.49	0.22	0.065	——
4	0.197	0.55	0.25	0.001	——
5	0.194	0.55	0.25	0.001	0.007

1, Reactions between ozone and bromine species only; 2, reaction of ozone and OH^- added; 3, reaction of ozone with 400 mM Cl^- added; 4, reaction between ClO^- and Br^- added; 5, phenol (0.1 uM), an oxidizable organic compound added to the model.

Ozone Reactor Sizing Model

$$\frac{\pi r^2 h}{Q} = 1 \text{ min} \qquad h = cr$$

Foam Fractionator Design Model

$$-\frac{d[DOC]}{dt} = \beta 1[DOC]$$

$$-\frac{d[PM]}{dt} = \beta 2[PM]$$

Mass DOC and PM per Day

$$m_{DOC} = (0.55 - 0.475p)F$$

$$m_{PM} = 0.45F$$


RK2
SYSTEMS

Future Work

- Ozone Kinetics Model Testing
- Foam Fractionation

“No aquarium, no tank in a marine land, however spacious it may be, can begin to duplicate the conditions of the sea”.

-Jacques Yves Cousteau

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