Webinar – April 25, 2013
Inland HAB Discussion Group

Advanced Oxidation Processes for the Destruction and Detoxification of Cyanotoxins

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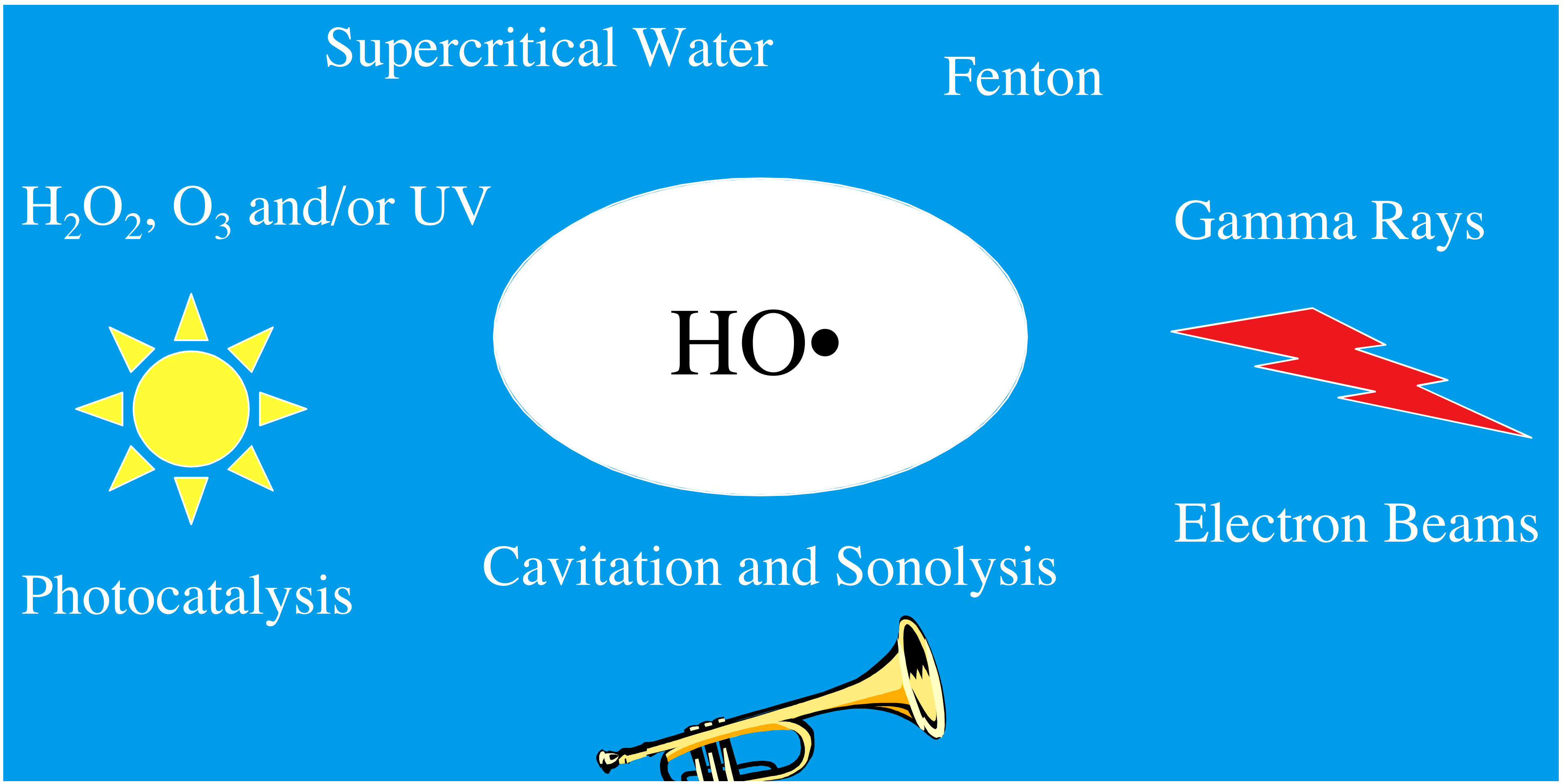
Outline

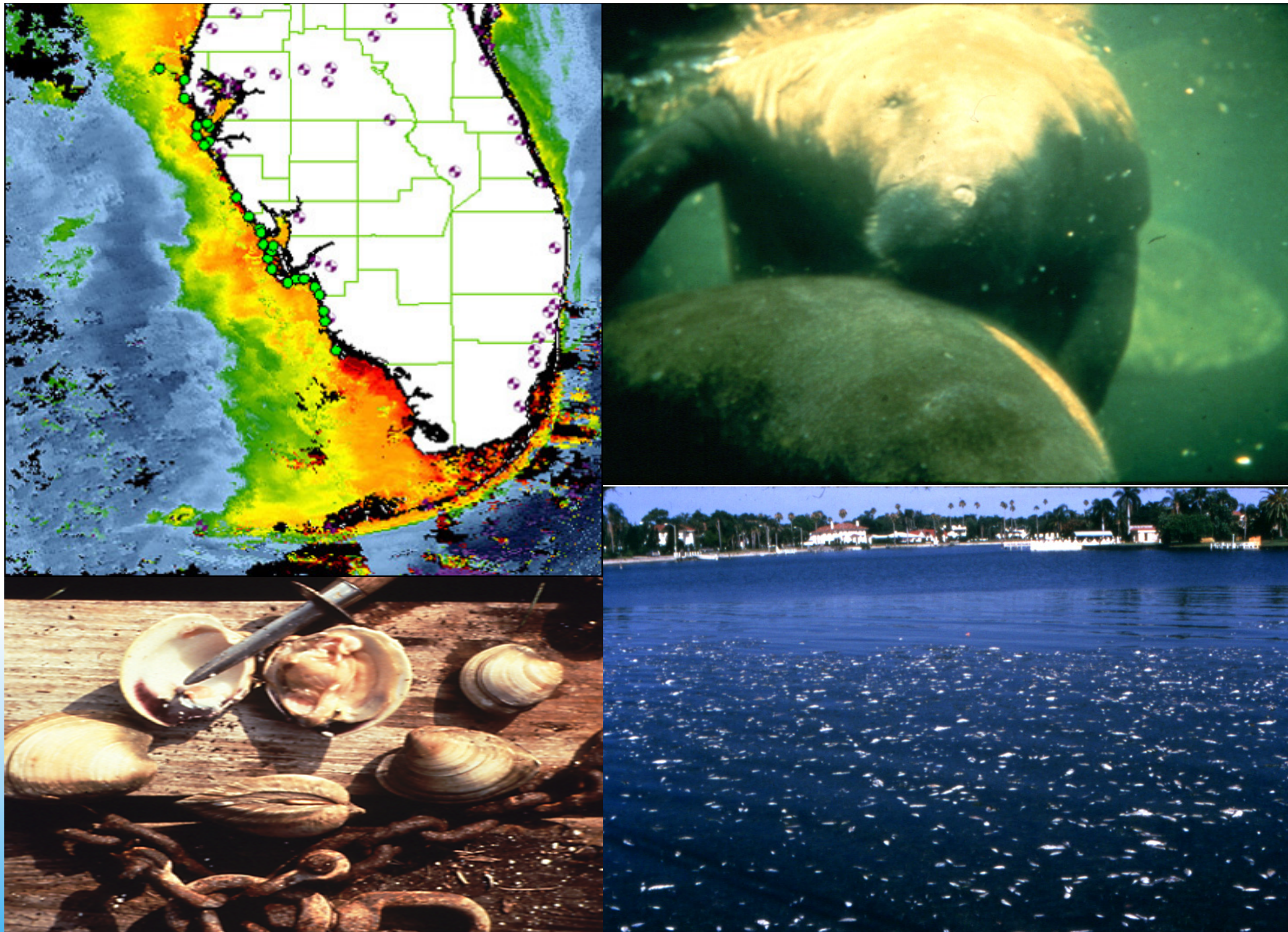
- Background - Advanced Oxidation Processes (AOP)
- HABs - Harmful Algae Blooms & Cyanotoxins
- Ultrasonic Destruction of Microcystin-LR
- Titanium dioxide Photocatalysis of Cylindrospermopsin
- Conclusions

Advanced Oxidation Technologies

Organic Toxin/Pollutant $\xrightarrow{\text{AOTs}}$ $CO_2 + H_2O + HX$



CyanoHAB Environmental Impact



Ray, S. M. ; Wilson, W. B. U.S. Fish Wildl. Serv. Bull. 1957, 123: 469-496
Bossart, G. D.; Baden, D. G.; Ewing, R. Y.; Roberts, B.; Wright, S. D. Toxicol. Pathol. 1998, 26:276-282.

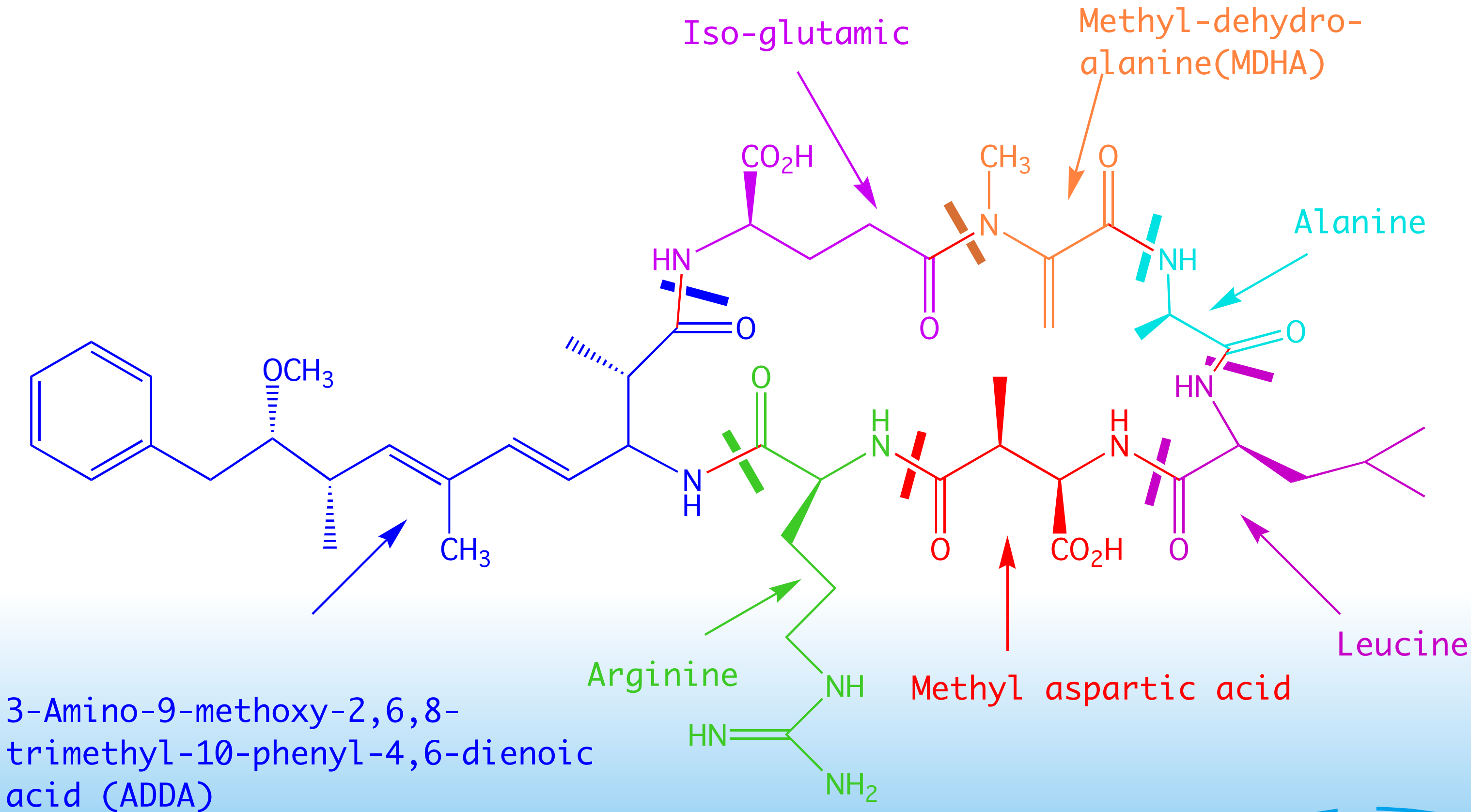
Harmful Algal Bloom


Marina in Port St Lucie, Florida following hurricane Katrina 2005

"Ultrasonically induced degradation of 2-methylisoborneol and geosmin", Weihua Song and Kevin E. O'Shea*, *Wat. Research* **2007**, *41*, 2672-2678

"The effects of ultrasound on cyanobacteria", Xiaoge Wu, Eadaoin M. Joyce, and Timothy J. Mason, *Harmful Algae*, **2011**, *10*, 738-743.

Microcystin-LR



$C_{49}H_{74}N_{10}O_{12}$ - HO• + C-H; k~10^{7-8} M^{-1} sec^{-1}

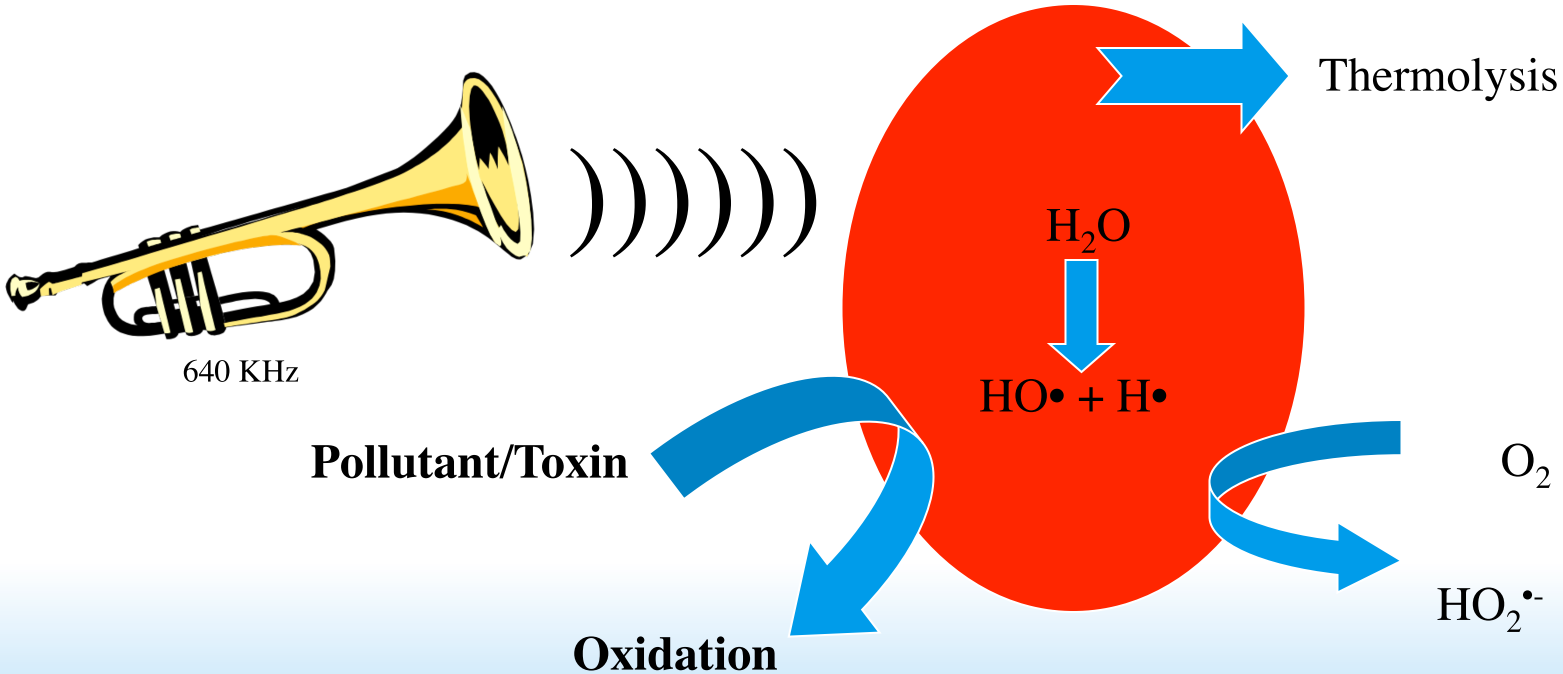
WHO, *Guidelines for drinking-water Quality*. ed.; World Health Organization: Geneva, **1998**

0.001 mg/litre (for total microcystin-LR, free plus cell-bound)

Degradation and Detoxification of MC-LR by Ultrasonic Irradiation

China Daily/Reuters/File

Ultrasonic Irradiation

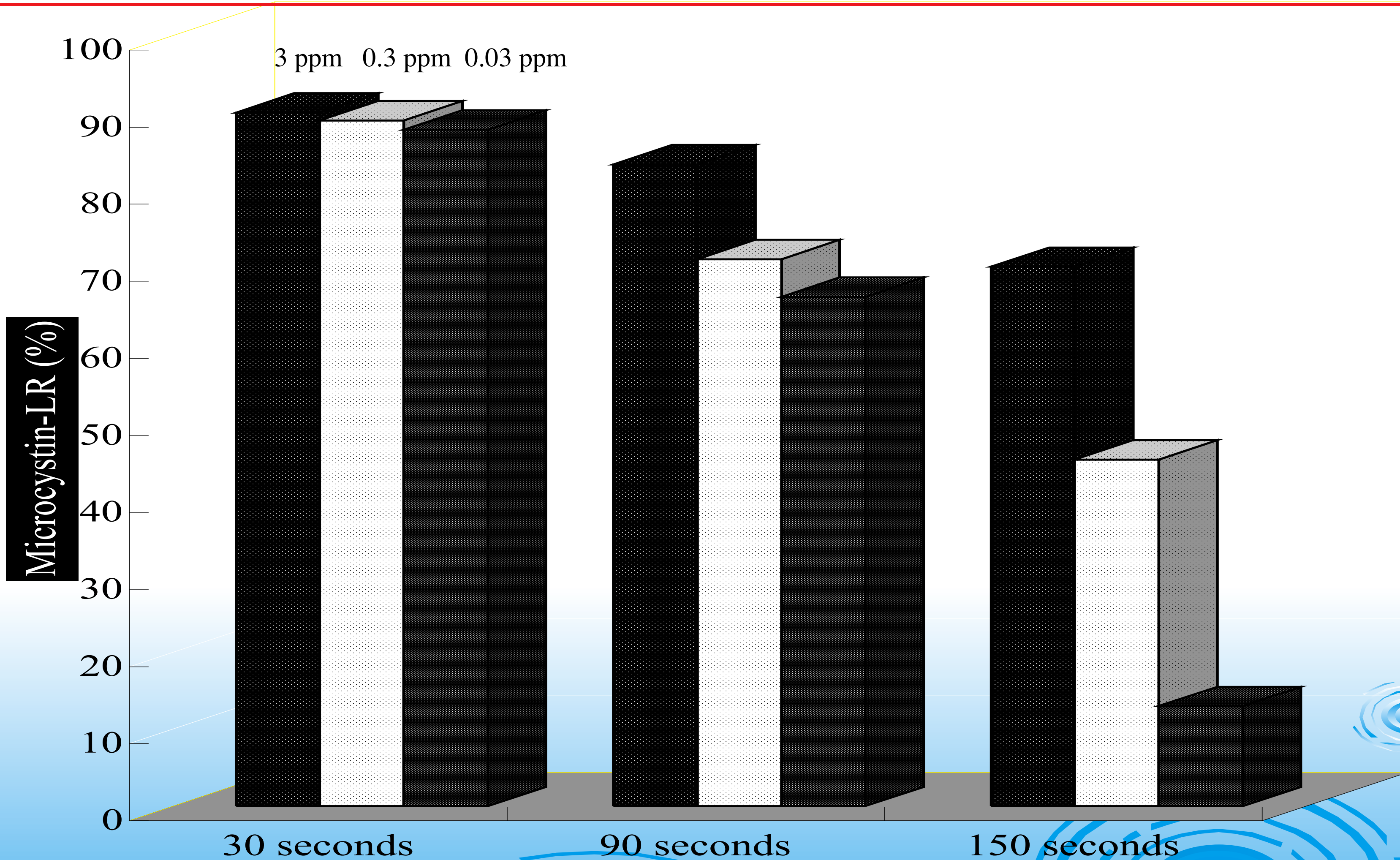


Reaction Zones

1) Vapor Region - Extreme Conditions Pyrolysis of water vapor and volatiles
2) Interface - Supercritical, (HO• + H•), Hydrophobic, LT Pyrolysis, hydrolysis
3) Bulk liquid - Limited to reactions of radicals diffusin from the interfacial region

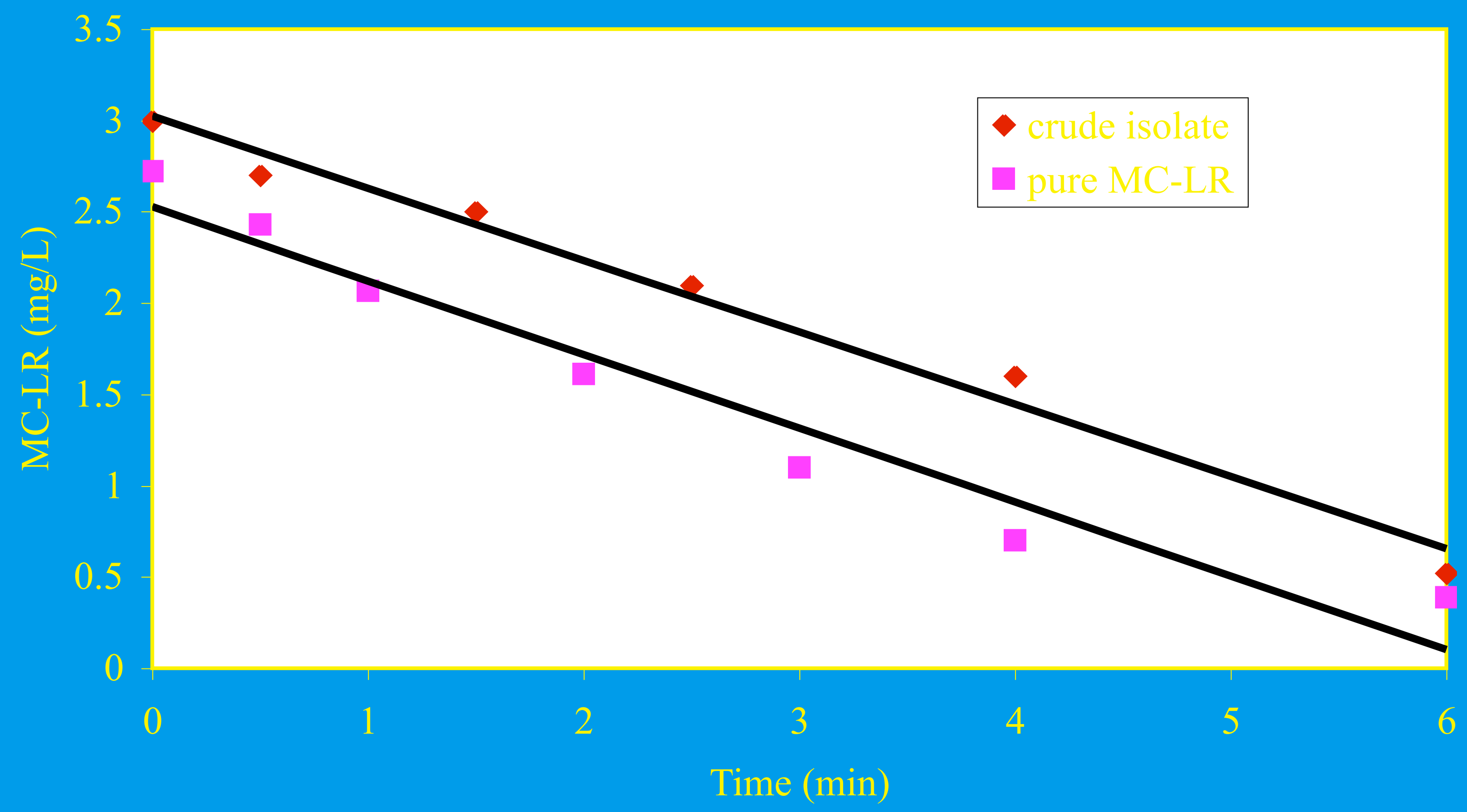
Mason, T. J. In *Sonochemistry and Sonoluminescence* Crum, L. A.; Mason, T. J.; Reisse, J. L.; Suslick, K. S. eds., Kluwer Academic, Dordreicht, **1999**, 363-370.

Ultrasonic Induced Degradation of Microcystin-LR

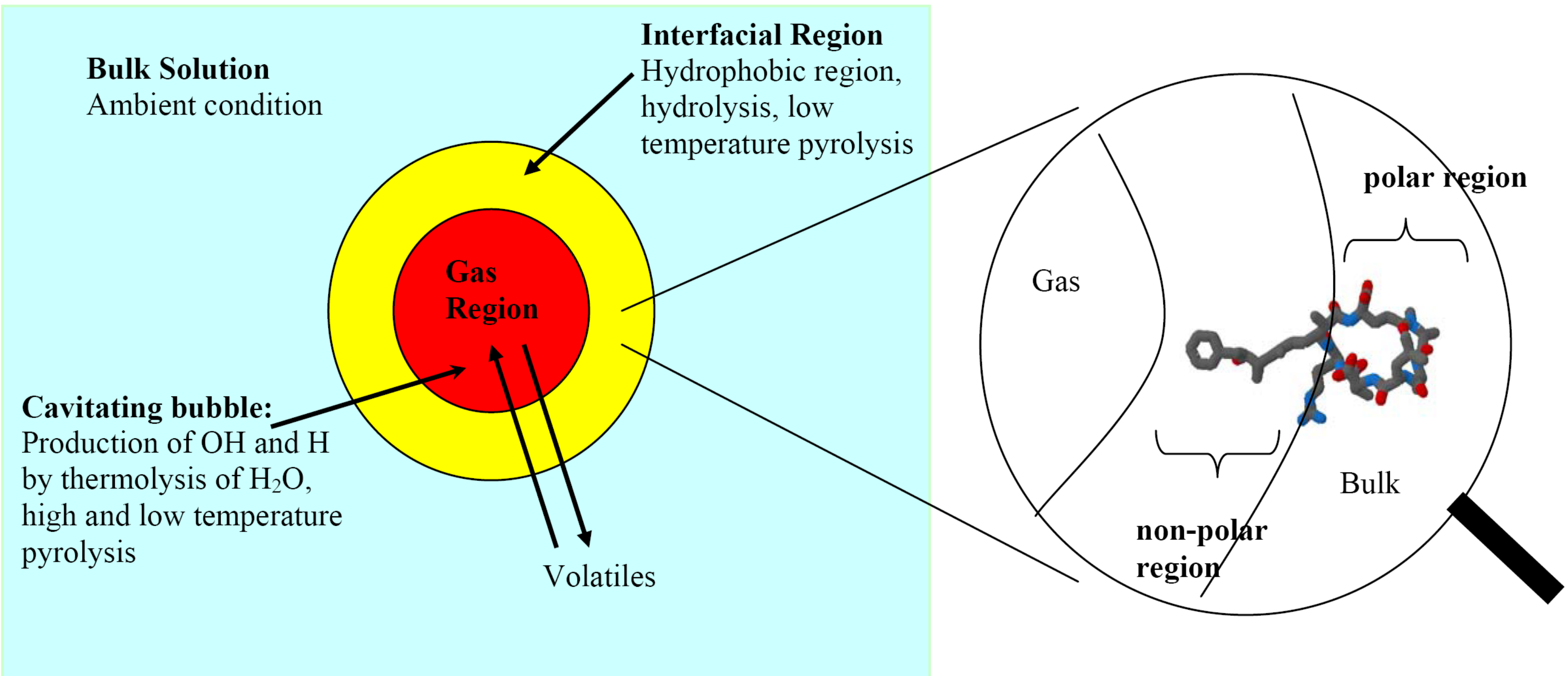


Weihua Song, Terri Teshiba, Kathleen Rein, and Kevin O' Shea, *Environ. Sci. Technol.* **2005**, *39*, 6300-6305.

Degradation of Crude and pure MC-LR



Ultrasonic irradiation of MC-LR



Evaluation of toxicity by brine shrimp assay

Without Ultrasonic Treatment

Concentration (ppm)	Number Exposed	Mortalities
0	35	0
1.6	20	6
3.1	20	10
6.25	29	22
12.5	27	24
25	50	48
50	50	50

LC50 = 3.01 ug/mL (1.98, 4.56)
95% confidence

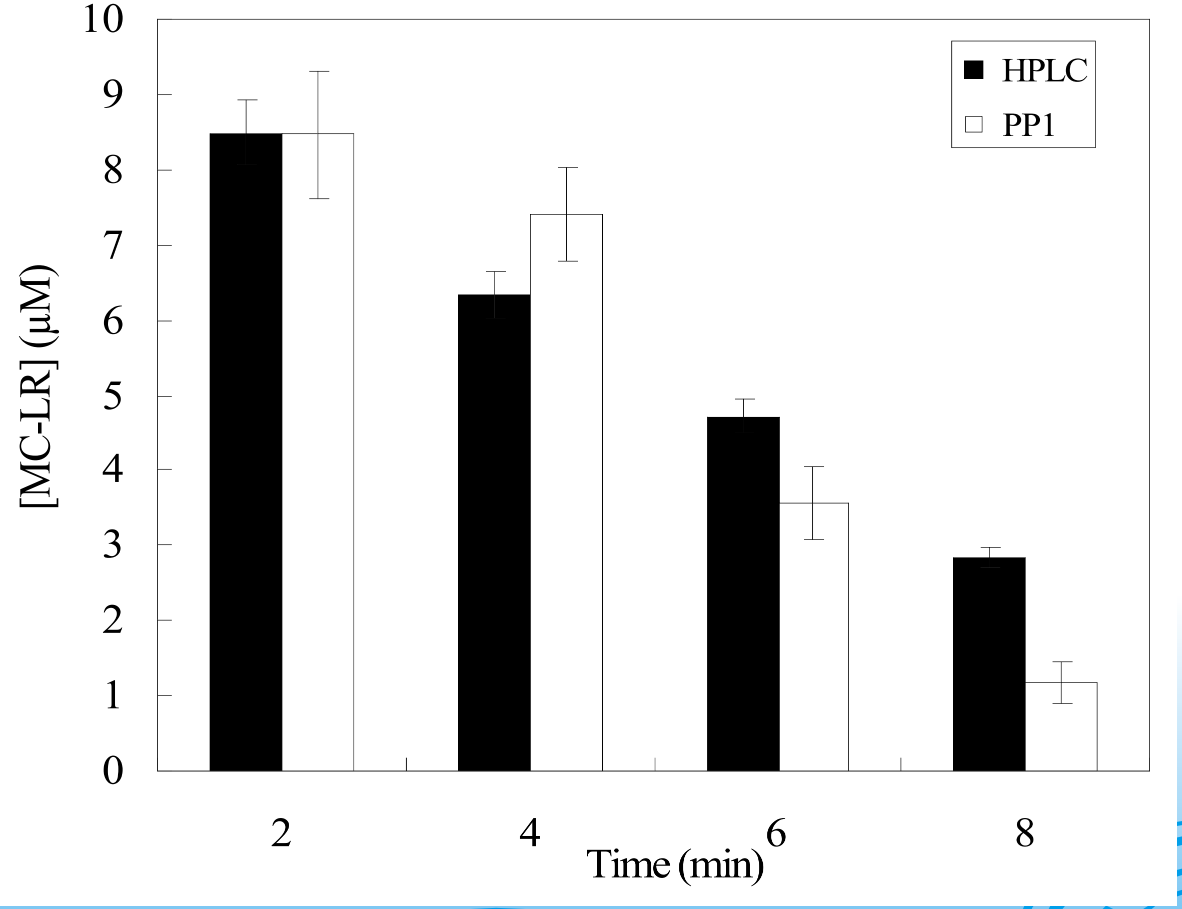
Ultrasonic Treatment (20 min)

Concentration (ppm)	Number Exposed	Mortalities
0	35	0
1.6	20	0
3.1	37	0
6.25	29	0
12.5	45	3
25	34	2
50	35	3

LC50 >> 50 ug/mL

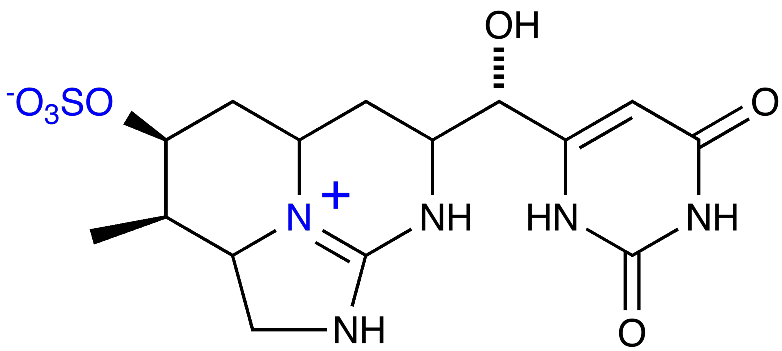
Alice Hudder, Weihua Song, Kevin E.O' Shea and Patrick Walsh *Toxicology and Applied Pharmacology,* **2007**

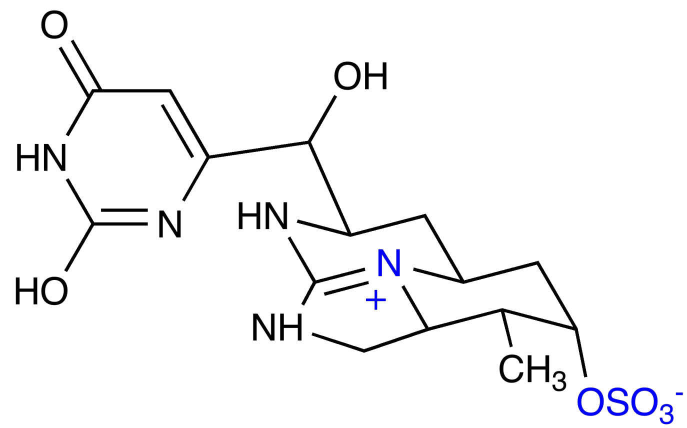
Detoxification of Microcystin-LR upon ultrasonic irradiation



Weihua Song, Terri Teshiba, Kathleen Rein, and Kevin O'Shea, *Environ. Sci. Technol.* **2005**, *39*, 6300-6305.

Cylindrospermopsin [143545-90-8]





([C15H21N5O7S]; mol. wt. = 415.43) Chemical name = 2,4(1*H*,3*H*)-Pyrimidinedione, 6-[(*R*)-hydroxy[2a*R*,3*S*,4*R*, 5a*R*,7*S*)-2,2a,3,4,5,5a,6,7- octahydro-3-methyl-4-(sulfoxy)-1*H*-1,8,8b-triazaacenaphthylen-7-yl]methyl]-, rel-(-)-

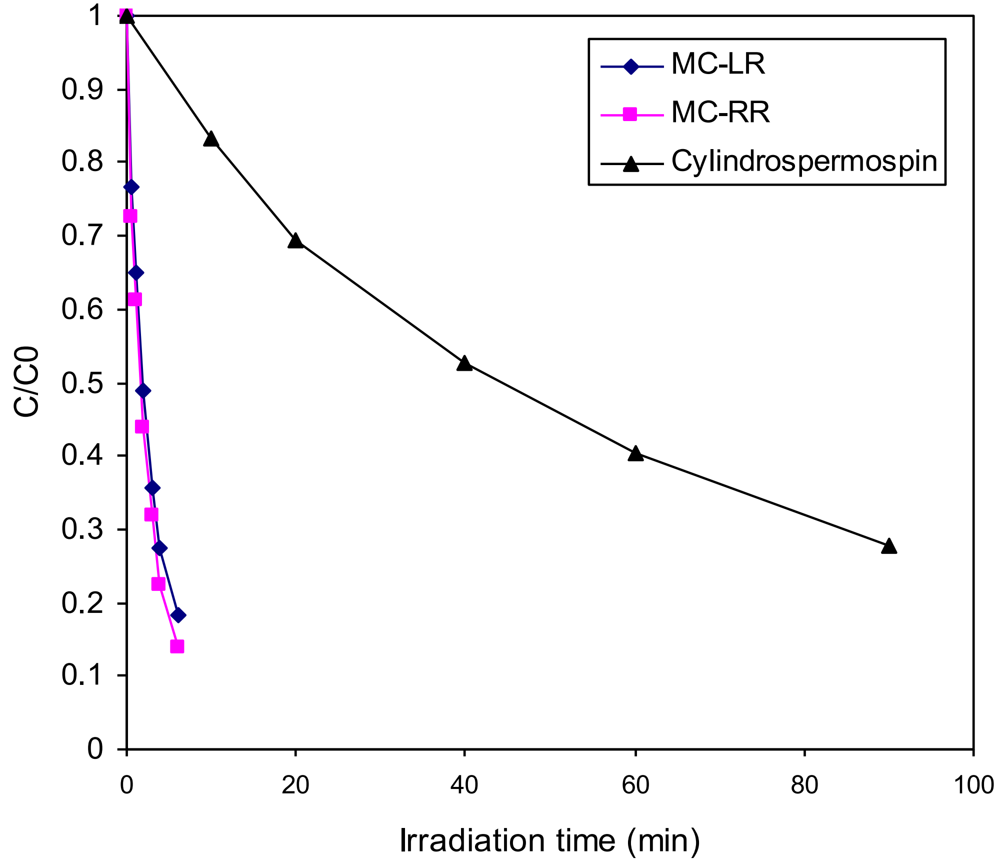
Cylindrospermopsin is relatively stable at extreme temperatures (no degradation at 100 °C for 15 minutes) and pH (~25% degraded at pH of 4, 7, and 10 for 8 weeks).

Toxic to liver and kidney, genotoxic and exhibits carcinogenic effects – Palm Island Mystery disease, Byth, S. 1980, Med. J. Aust., 2, 40-42.

Not effectively treated by traditional waste water treatments

J.Am.Chem.Soc.**1992**.114(20): 7941-7941, Terao, K. *Toxicon* 32, 73-84. **1994**, Falconer, I.R., Humpage, A.R, *Environ. Toxicol*. 16, 192-195. **2001**

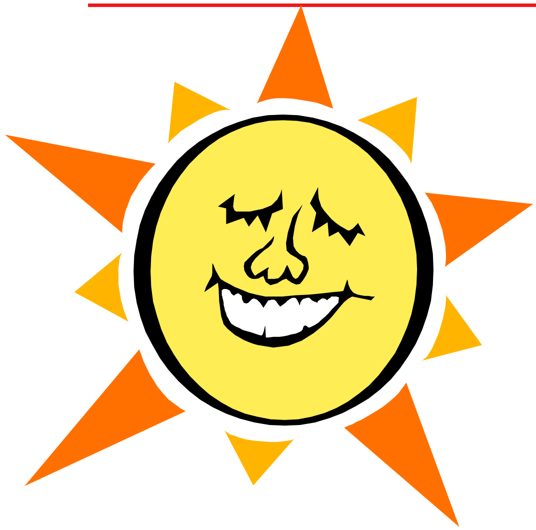
Ultrasonic Induced Degradation of CYN and MCs

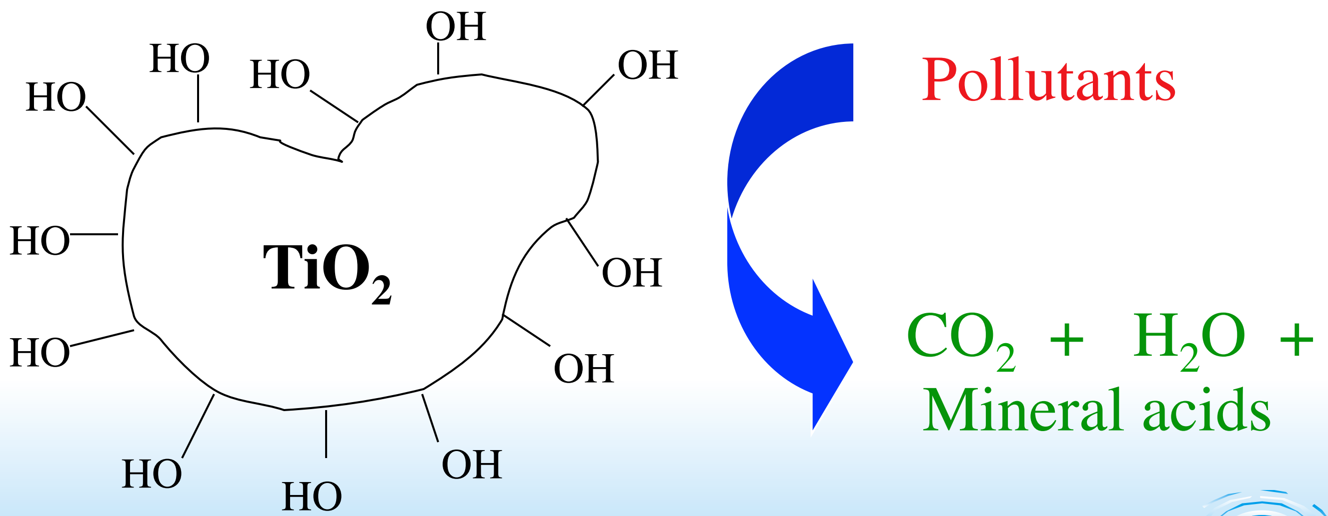


Degradation of CYN and MCs by ultrasound; 640 KHz, air saturated, initial concentrations 4-5 ppm

Weihua Song, Terri Teshiba, Kathleen Rein, and Kevin O'Shea, *Environ. Sci. Technol*. **2005**, *39*, 6300-6305.
Weihua Song, Armah A. De La Cruz, Kathleen Rein, and Kevin E. O'Shea, Environ. Sci. Technol. **2006**, 40,3941-3946
Alice Hudder, Weihua Song, Kevin E. O'Shea and Patrick Walsh *Toxicology and Applied Pharmacology,* **2007,** 220(3), 357-364.

Solar Powered Decontamination

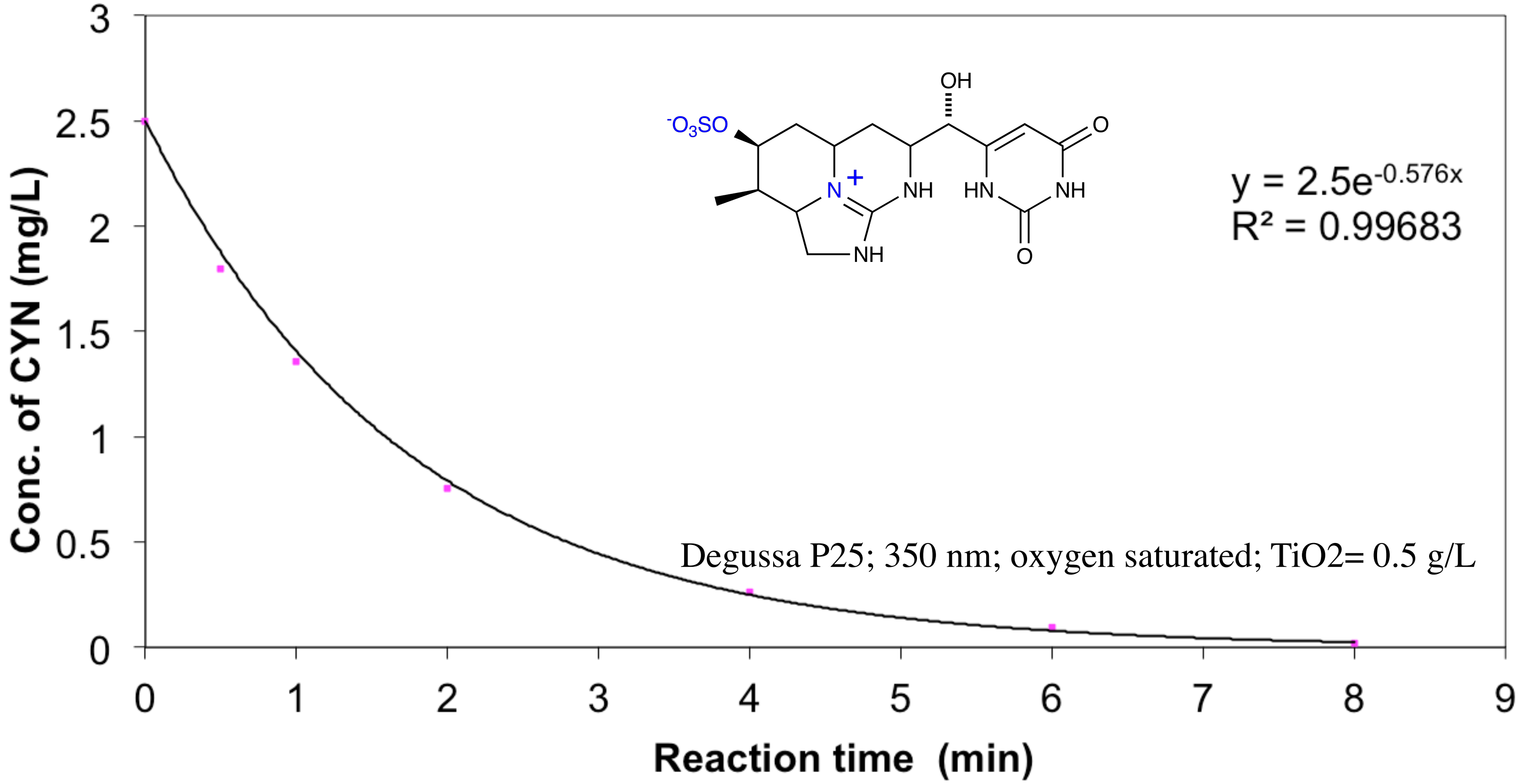




D.F. Ollis, E. Pelizetti, and N. Serpone, *Environ. Sci. Technol.* **1991**, 25, 1523
M.A. Fox and M.T Dulay, *Chem. Rev.* **1993**, *93*, 341; P.V. Kamat, *Chem. Rev.* **1993**, *93*, 267.
M.R. Hoffman, S.T. Martin, W. Choi, and D.W. Bahnemann, *Chem. Rev*, **1995**, *95*, 69

"Mechanistic Evaluation of Arsenite Oxidation", Tielain Xu, Prashant V. Kamat and Kevin O' Shea, *J.Phys. Chem. A* 2005, *109*, 9070-9075.
UV and solar TiO2 photocatalysis of brevetoxins (PbTxs), *Toxicon* 2010, 1008-1016.
Synthesis, structural characterization of sol-gel based NF-TiO2 films with VLA for removal of MC-LR M. Pelaez, P. Falaras, V. Likodimos, A. Kontos, A. Cruz, Kevin O'Shea, D. Dionysiou *Applied Cata B: Enviro* 2010, 99, 378.

UV TiO_2 photocatalysis of CYN



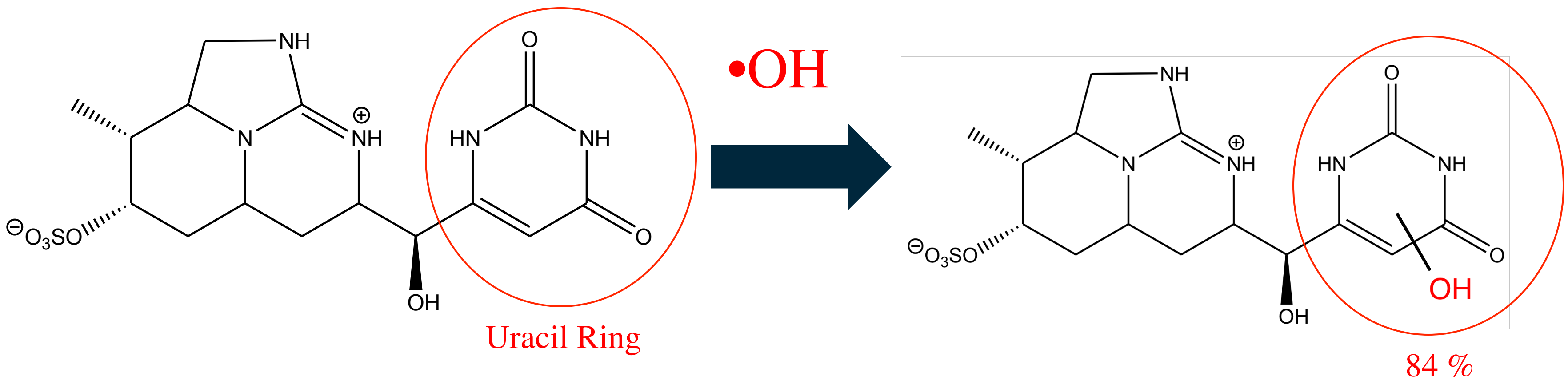
<u>Previous Reports on UV TiO2 Photocatalysis</u>

Senogels, P. J., Shaw, S. J. A., Stratton, H., (2001). Photocatalytic degradation of the cyanotoxin cylindrospermopsin, using titanium dioxide and UV irradiation. Wat. Res. 35(5): 1245-1255.

Jaussaud, C., Paisse, O., and Faure, R., (2000) Photocatalysed degradation of uracil in aqueous titanium dioxide suspensions: mechanisms, pH and cadmium chloride effects. *J. Photochem. Photobiol., A*, 130(2-3), 157-162.

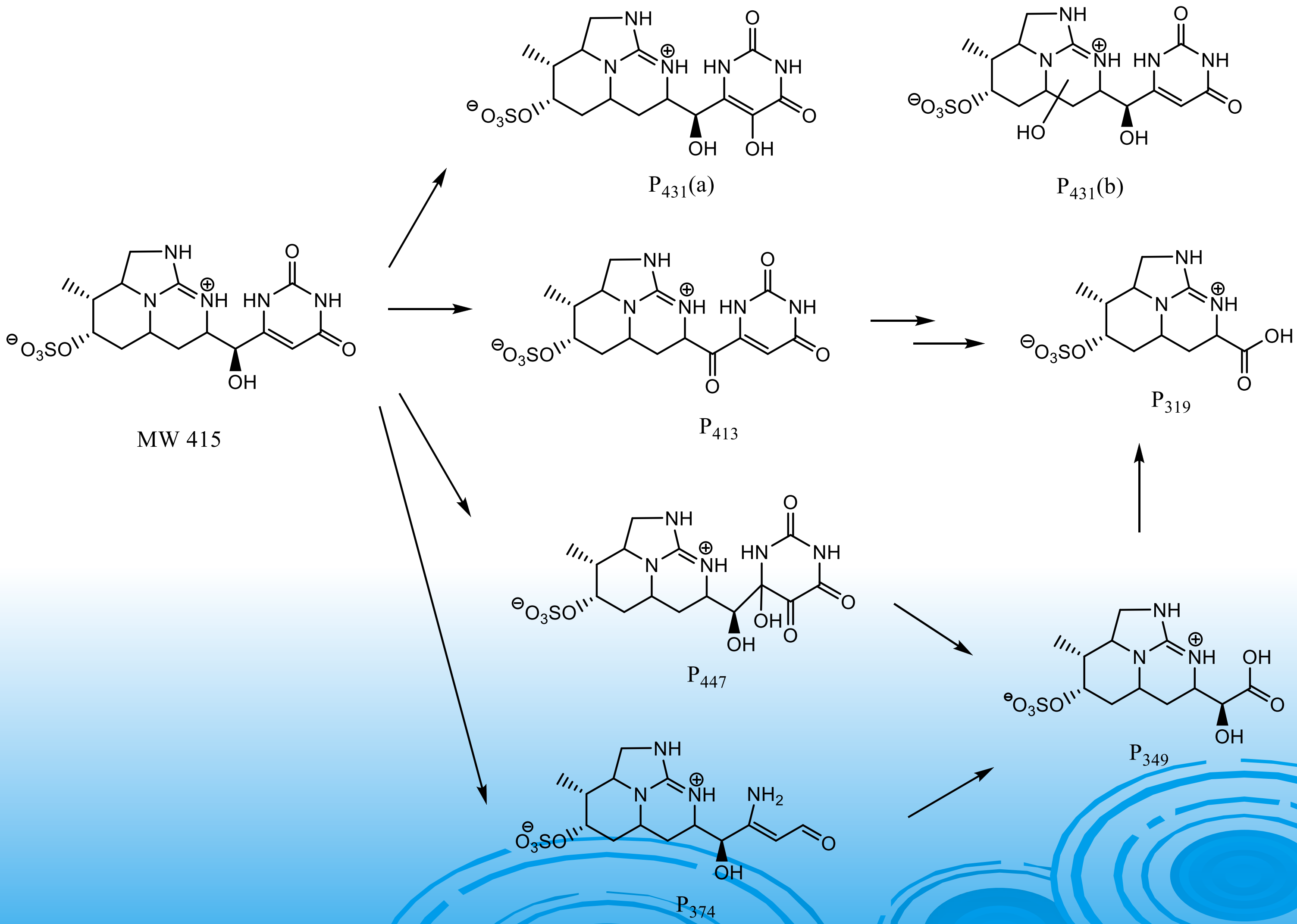
Summary of Reactivity of CYN with HO•

$H_2O \rightarrow$ (0.28)•OH + (0.06)H• + (0.27)e^-_{aq} + (0.05)H_2 + (0.07)H_2O_2 + (0.27)H^+



	k_{OH} (M^{-1} s^{-1})
Uracil CYN	(5.7×10^9) average of 7 literature values ($(5.08 \pm 0.16) \times 10^9$) (overall)
Growth transient	$(4.75 \pm 0.02) \times 10^9$ (4.75/5.08) => 84 %

Degradation products and proposed reaction pathways for •OH + CYN



Hydroxyl Radical Oxidation of CYN and its role in the Photochemical Transformation, Weihua Song, Shuwne Yan, William J. Cooper, Dionysios Dionysiou, Kevin O'Shea, Environ. Sci. Tech, 2012, 46, 12608-12615.

Conclusions

- Ultrasonic treatment of microcystin-LR (MCLR) results in the predominant and selectively oxidation of the ADDA diene and aromatic ring leading to detoxification even in the presence of dissolved organic material. Taste and odor compounds associated with HABs are also readily degraded.
- PP1 and Brine shrimp assays indicate the oxidation products produced from advanced oxidation of MCs are not toxic.
- AOPs should be effective for all ADDA chain containing MC variants (> 80) and nodularins.
- Cylindrospermopsin, a charged species, is more effectively degraded by titanium dioxide photocatalysis than ultrasonic irradiation. Ultrasonic induced destruction may be particularly attractive for treatment of hydrophobic toxins, while photocatalysis may be more effective for polar and charged species.
- The initial water quality and treatment objectives are critical in determining the feasibility of real applications of different AOPs. Treatment trains, for example careful separation of algal cells, subsequent treatment with an AOP and bioremediation, also need to be consider among treatment options.

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