Understanding Algal Blooms: State of the Science Conference

Toledo, Ohio. September 15, 2016

Treatment of Cyanotoxin Microcystin-LR by Advanced Oxidation Technologies

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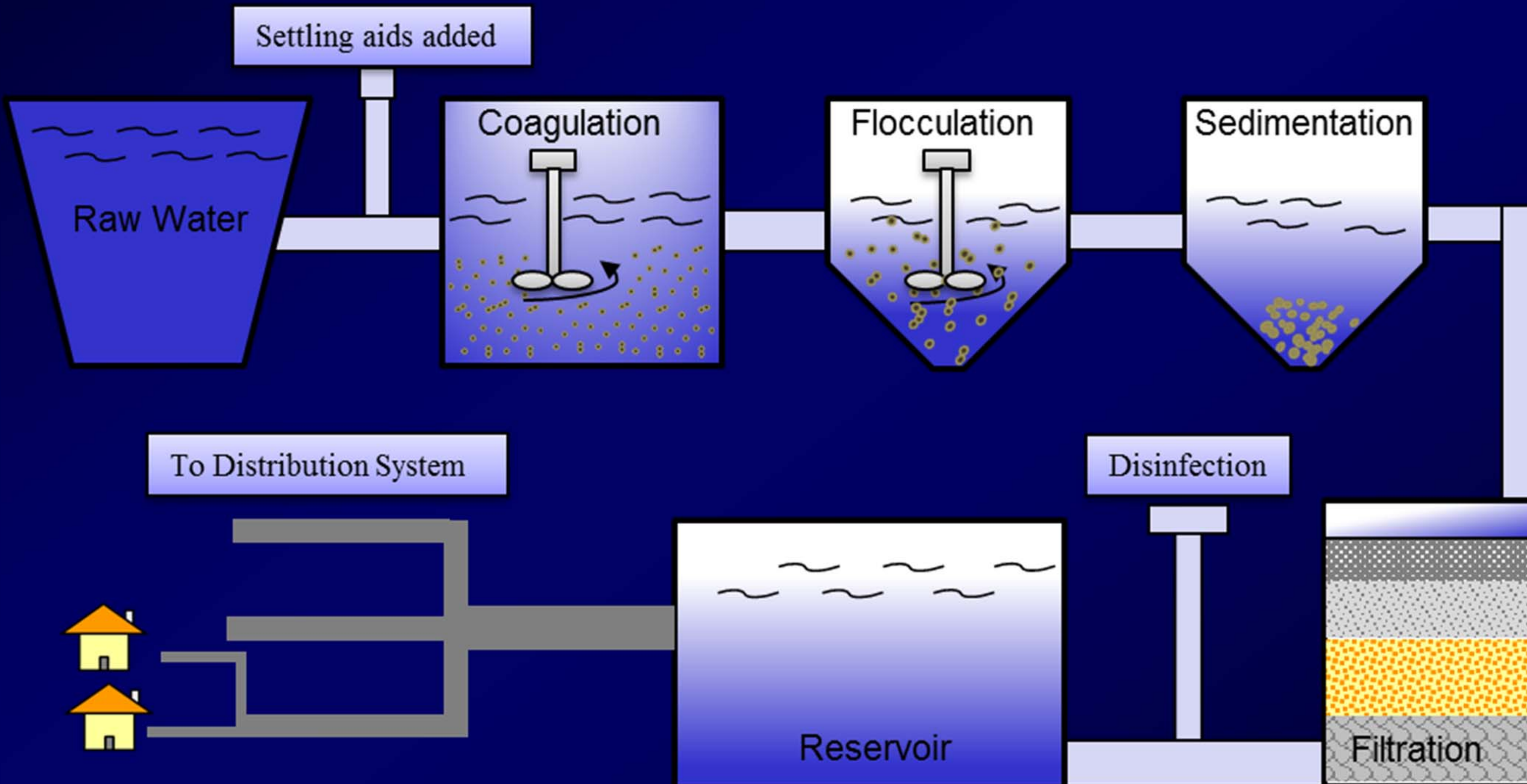
The project was supported by a Harmful Algal Bloom Research Initiative grant from the Ohio Department of Higher Education.

OHIO SEA GRANT

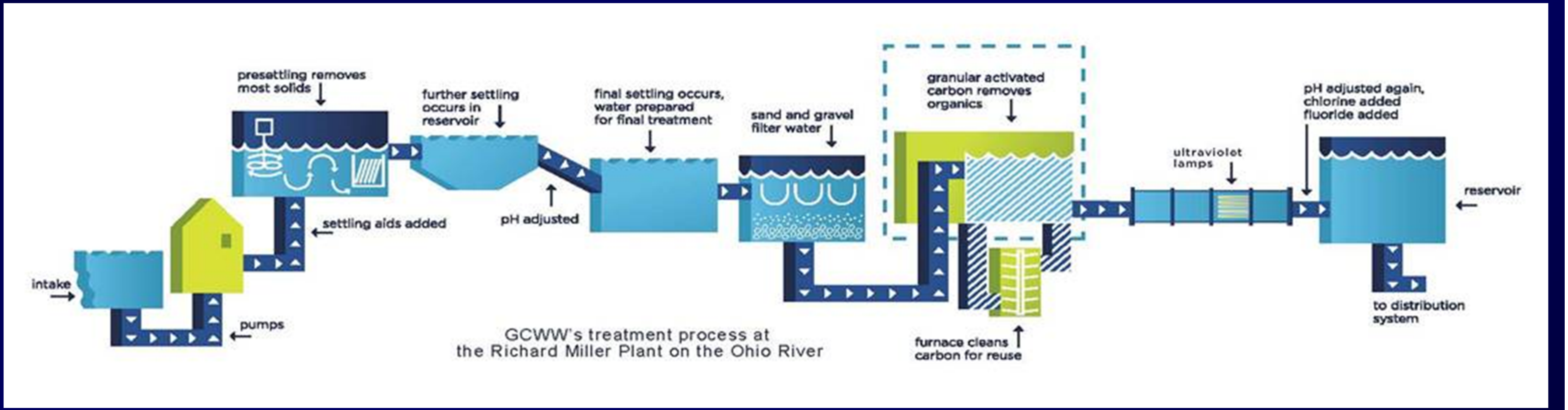
Some of the work presented in the conference has not been published and was not included. Feel free to contact Dr. Dionysios D. Dionysiou (*dionysios.d.dionysiou@uc.edu*) if additional information is needed.

Example of Common (Conventional) Water Treatment Process



Example of Treatment Plant with Additional Unit Processes

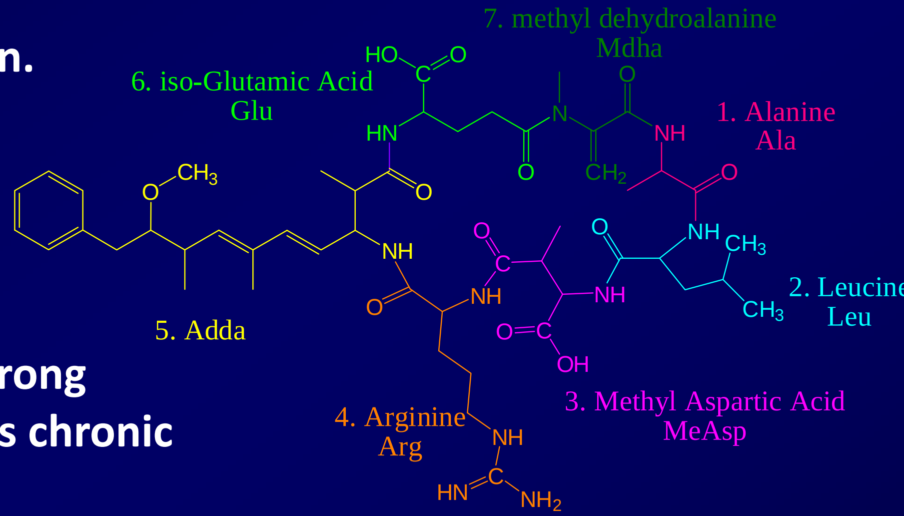
- **Richard Miller Treatment Plant, Greater Cincinnati Water Works (GCWW)**



http://www.cincinnati-oh.gov/water/about-greater-cincinnati-water-works/water-treatment/

Microcystin-LR (MC-LR)

- The most widespread and toxic cyanotoxin.
- High chemical stability (cyclic structure)
- Very Soluble in water (functional groups)
- $LD_{50,\ MCLR}$ = 50 µg/Kg (mouse bioassay). Strong hepatotoxicity. Even at low concentrations chronic MC-LR exposure can induce liver cancer.



- The health advisory values issued by EPA:
  - 0.3 µg/L for children younger than school age
  - 1.6 µg/L for all other ages

H. Ufelmann, et al., Toxicology, 293 (2012) 59-67.
N.Q. Gan, et al., Chem Res Toxicol, 23 (2010) 1477-1484.
Y.F. Fang, et al., Environmental Science & Technology, 45 (2011) 1593-1600.

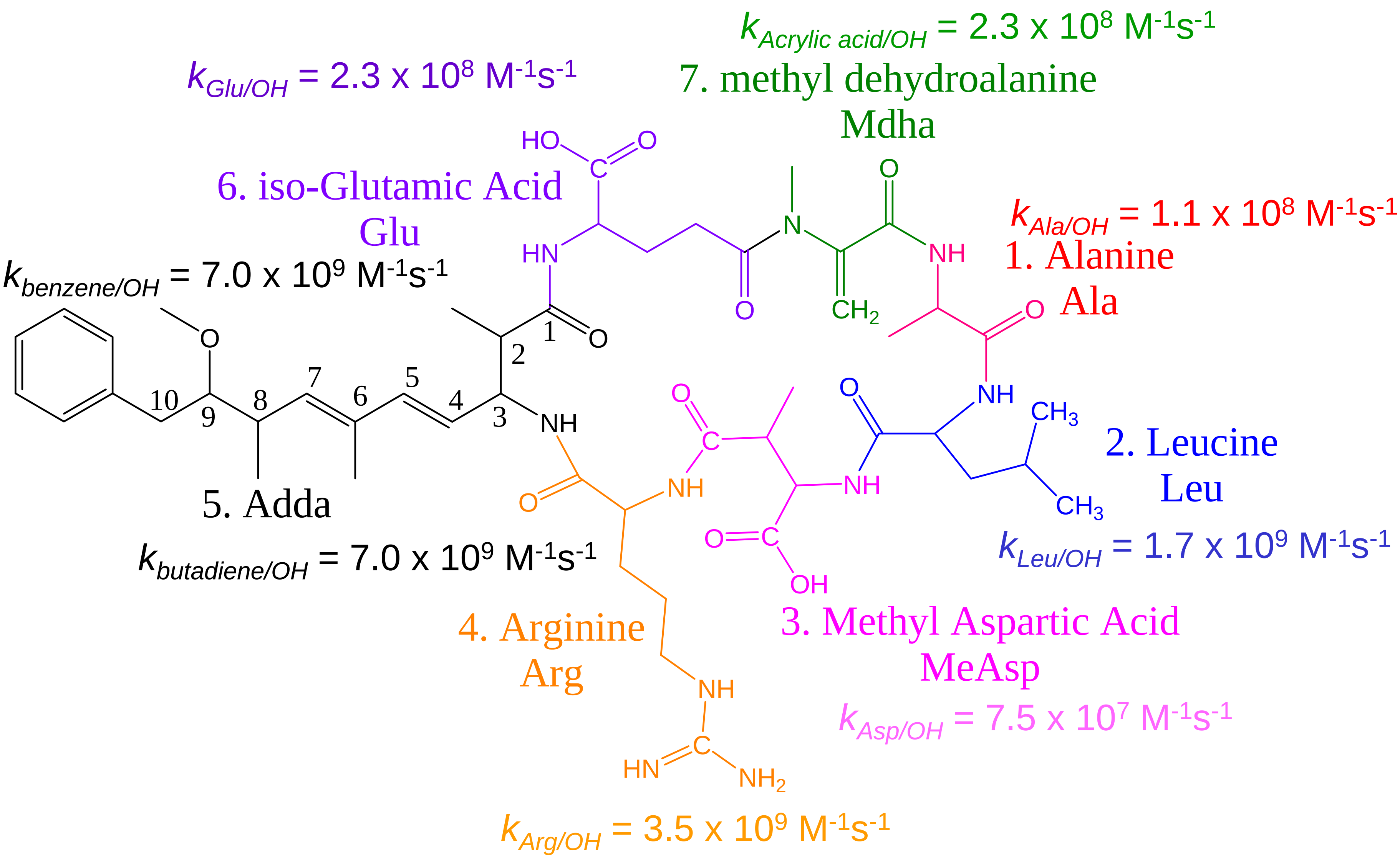
Advanced Oxidation Technologies (AOTs)

- **Chemical Oxidation (O_3 high pH, O_3+H_2O_2, Fe^{2+}+H_2O_2)**
- **Photo Fenton Processes (Fe^{2+}+H_2O_2+UV)**
- **UV+O_3 , UV+H_2O_2 , UV+O_3+H_2O_2**
- **Photocatalytic Redox Processes (i.e., TiO_2 Photocatalysis)**
- **Electron Beam and γ-Irradiation**
- **Supercritical Water Oxidation**
- **Sonolysis**
- **Non-Thermal Plasmas**

Common Characteristic:

Generation of Hydroxyl Radicals ($^{\bullet}OH$)

Second order rate constants ($k_{x/OH}$) with the amino acids of MC-LR

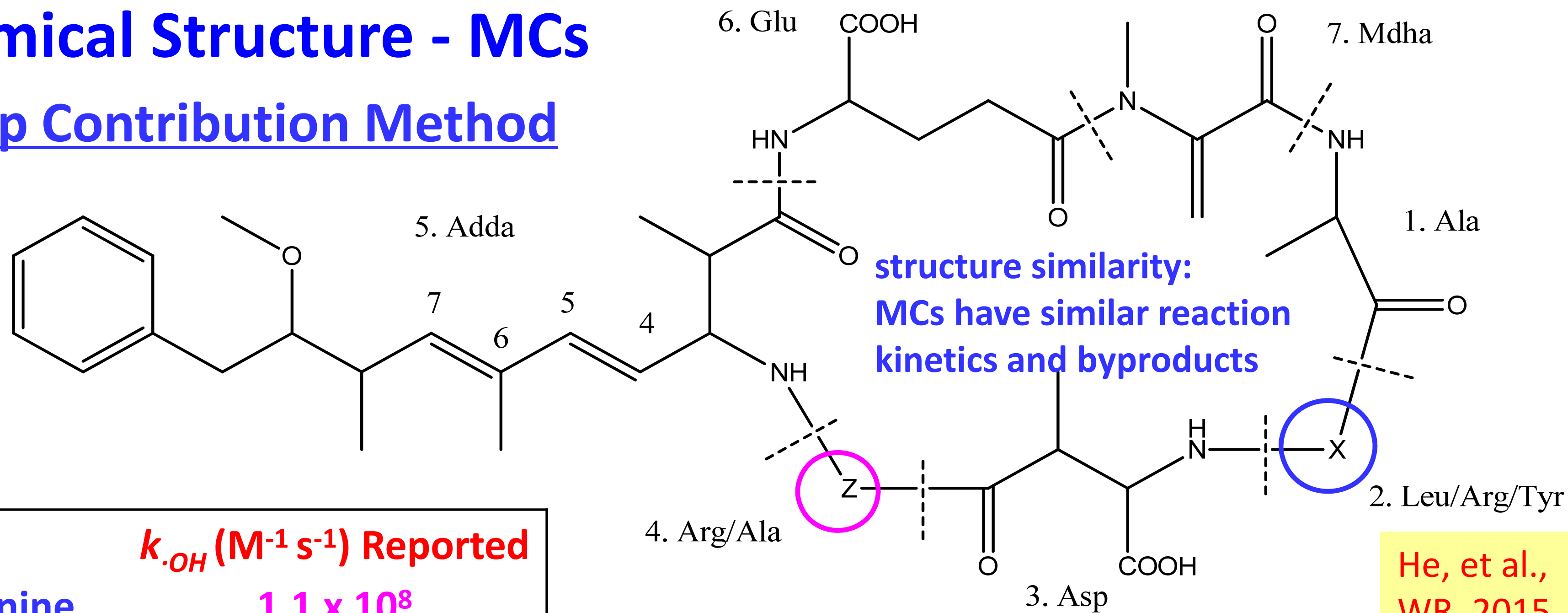


Overall rate constant of HO• addition > 1.0×10^{10} $M^{-1}s^{-1}$

Song *et al.*, *Environ. Sci. Technol*, 43 (2009) 1487

Chemical Structure - MCs

Group Contribution Method



structure similarity:
MCs have similar reaction kinetics and byproducts

He, et al., WR, 2015

	$k_{\cdot OH}$ (M^{-1} s^{-1}) Reported
Alanine	1.1 x 10^{8}
Arginine	3.5 x 10^{9}
Leucine	1.7 x 10^{9}
Tyrosine	1.3 x 10^{10}

Both theoretical and measured order of $k_{\cdot OH}$:
YR > RR > LR > LA

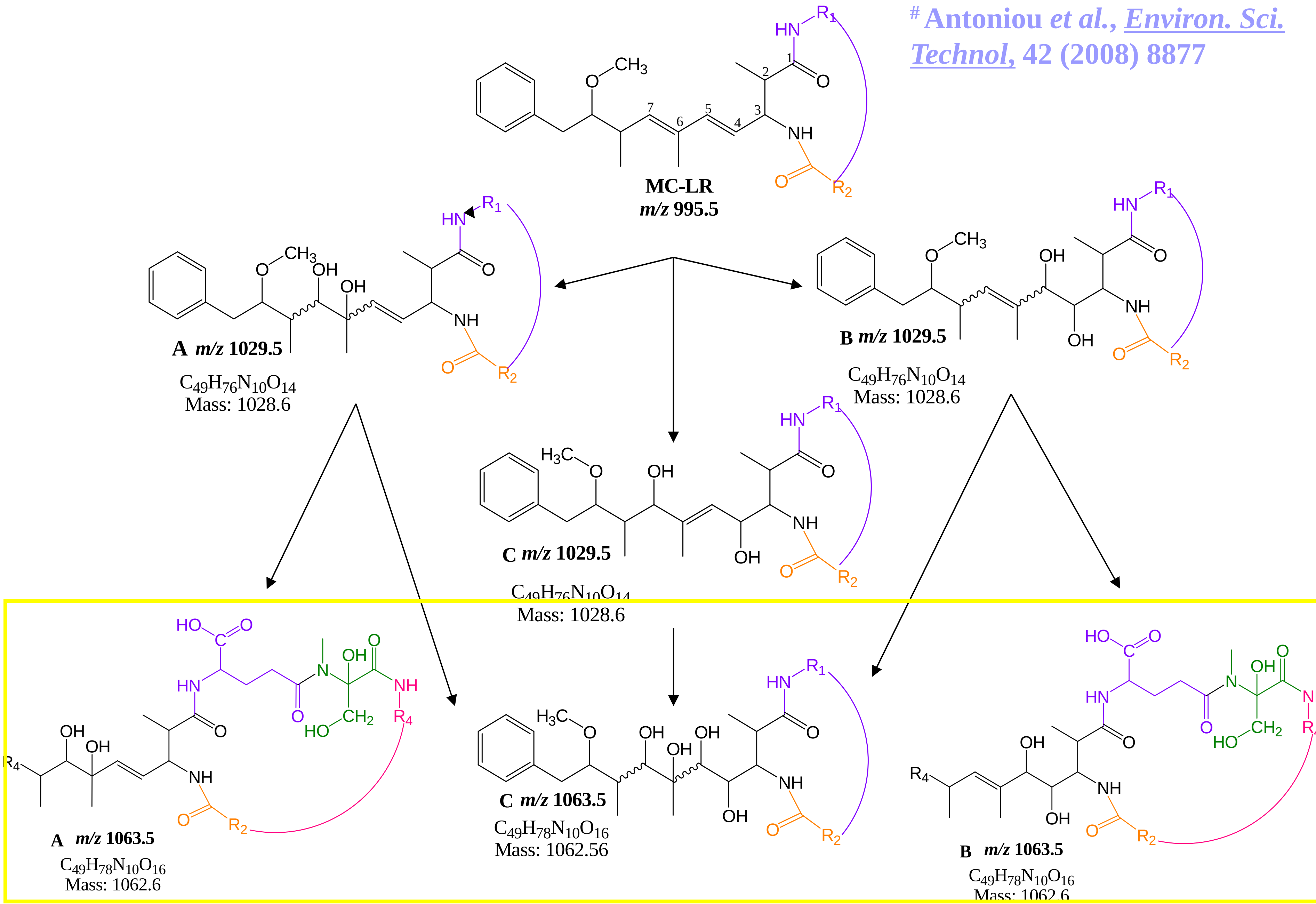
	X	Y	$k_{\cdot OH}$ (M^{-1} s^{-1}) (X+Y)
MC-YR	Tyrosine	Arginine	1.65x 10^{10}
MC-RR	Arginine	Arginine	7.0 x 10^{9}
MC-LR	Leucine	Arginine	5.2x 10^{9}
MC-LA	Leucine	Alanine	1.8x 10^{9}

	Measured Second-Order Rate Constant $k_{\cdot OH}$ ($x10^{10}$ M^{-1} s^{-1})
MC-YR	1.66
MC-RR	1.30
MC-LR	1.06
MC-LA	0.98

http://www.cyanobacteria-platform.com/cyanotoxins.html, Antoniou, 2008.*Environ. Sci. Technol*, 42:8877. Song , 2009. *Environ. Sci. Technol*, 43: 1487. Buxton, 1988. J. Phys. Chem. Ref. Data, 17(2):513-886. Daisuke, 2009. Environ. Sci. Technol. 43: 6220-6227.

•OH Attack: Site C: Diene Bonds with HRs#

[#] Antoniou *et al.*, *Environ. Sci. Technol*, 42 (2008) 8877



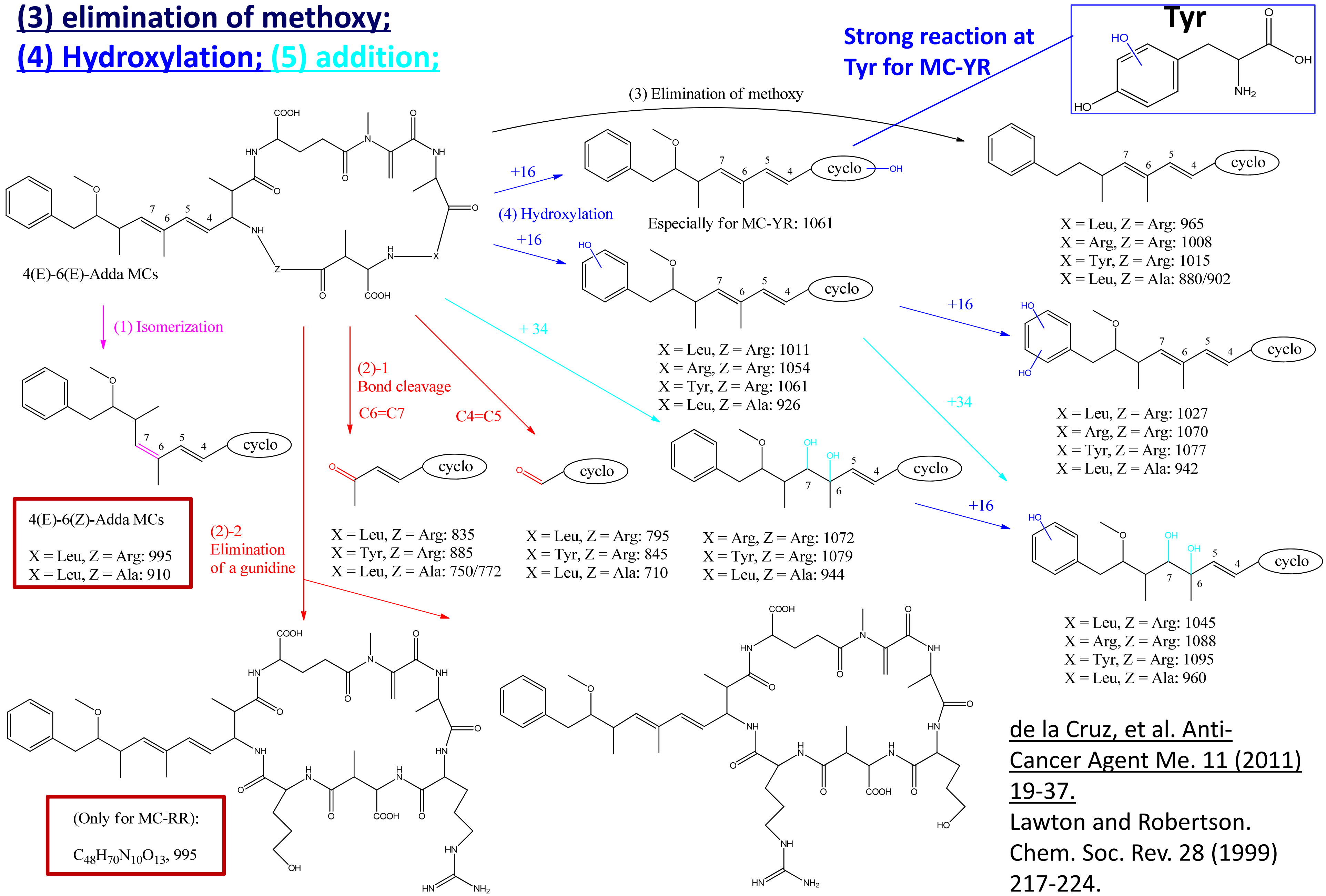
Transformation of MCs by •OH: influence of amino acid variable

He, et al. WR, 2015

(1) Isomerization (LR, RR); (2)-1 bond cleavage (LR, YR, LA); (2)-2 guanidine removal (RR)

(3) elimination of methoxy;

(4) Hydroxylation; (5) addition;



de la Cruz, et al. Anti-Cancer Agent Me. 11 (2011) 19-37.

Lawton and Robertson. Chem. Soc. Rev. 28 (1999) 217-224.

Key Point

$HO^{\bullet}$ is very reactive with Microcystins and ultimately breaks them down step by step to smaller reaction products that do not exhibit hepatotoxicity

UV-Based Advanced Oxidation Technologies (UV-AOTs)

- H_2O_2: $H_2O_2 + hv \rightarrow {}^{\bullet}OH + {}^{\bullet}OH$ $(\phi = 1.0)$
- Cl_2: $HOCl/OCl^{-} + hv \rightarrow {}^{\bullet}OH + Cl^{\bullet}$ $(\phi > 1.0)$

UV Collimated Beam Unit

LP UV lamps

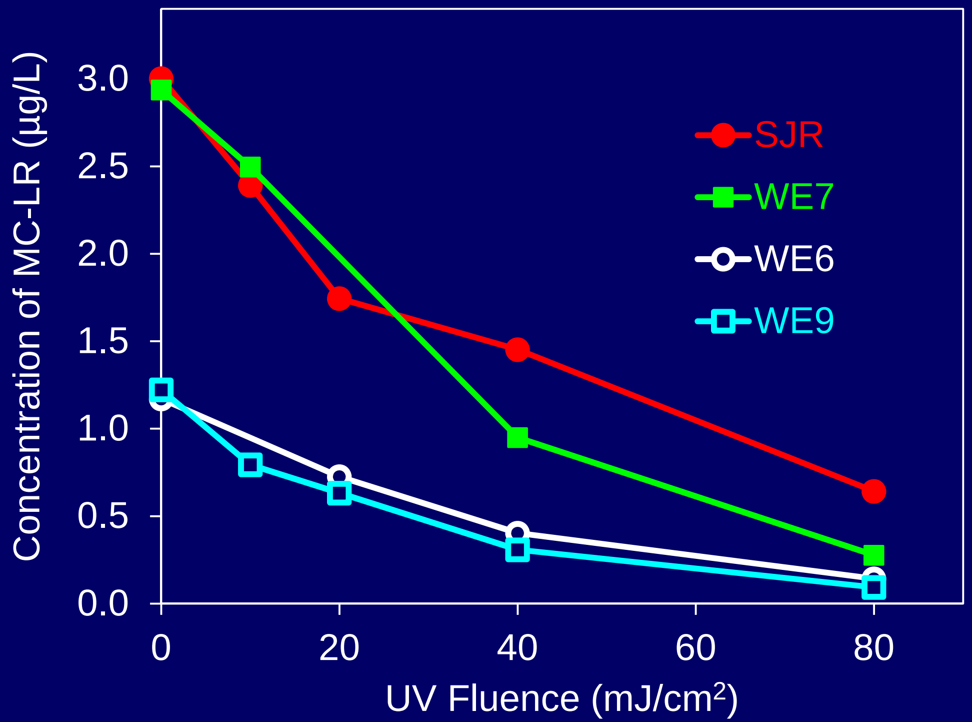
(l_{max} @ 254 nm)

UV fluence rate = 0.1 mW/cm^2

UV-LED (255 nm, 285 nm, 365 nm)

Removal of Low Concentration Level of MC-LR by UV/H_2O_2 From Real Water Samples

He et al, WR, 2012



- **ELISA Analysis**

At the UV fluence of 80 mJ/cm^2,

For the initial concentration levels ranging from 1.0 μg/L to 3.0 μg/L,

Final concentration below 1.0 μg/L could be achieved by UV/H_2O_2 even when using real water samples.

	SJR	*WE7*	*WE6*	*WE9*	SQ-1	SQ-2
Initial Concentration of MC-LR (μg/L)	3.00	2.94	1.17	1.22	2.59	1.00
Final [MC-LR] @ 80 mJ/cm^2	0.64	0.28	< 0.147	< 0.147	< 0.147	< 0.147

Acknowledgement

- The study was mainly conducted by Dr. Maria Antoniou, Dr. Xuexiang He, and Ms. Xiaodi Duan.

- The project was supported by a Harmful Algal Bloom Research Initiative grant from the Ohio Department of Higher Education.