

Cyanotoxins and Drinking Water

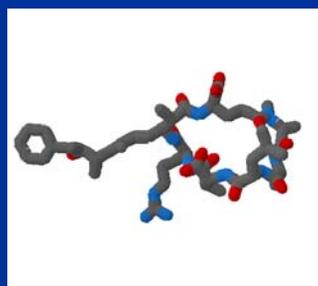
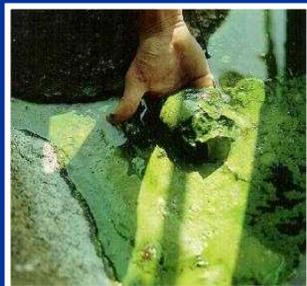
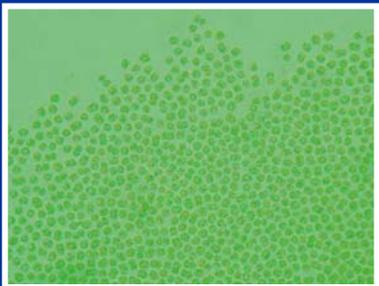
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May 2007

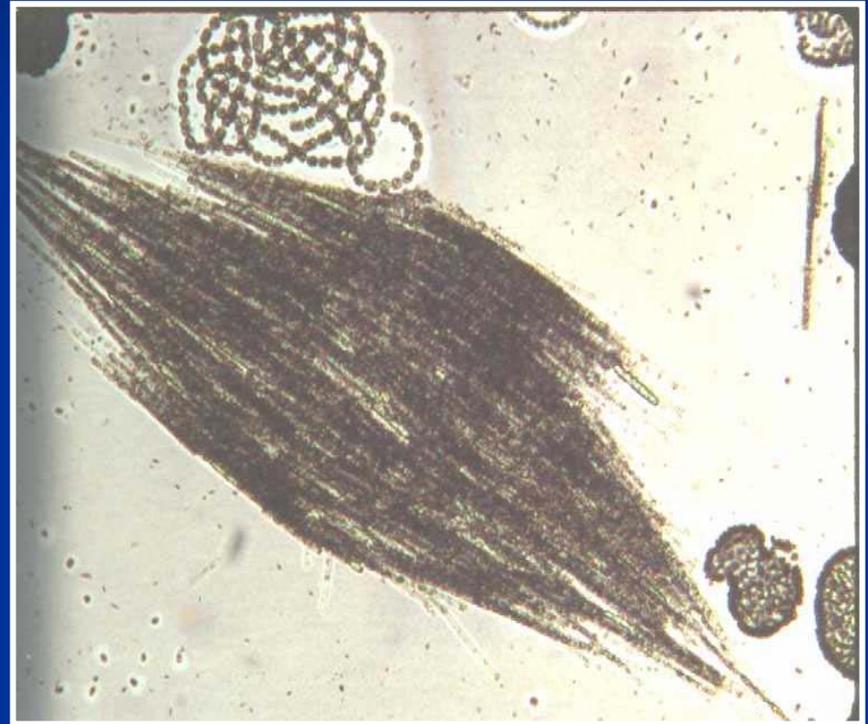


Cyanobacteria (Blue-Green Algae)

Fresh water toxins are produced by cyanobacteria



Cyanobacteria bloom



Mixture of cyanobacteria

Cyanotoxins



- There are over 70 different cyanotoxins
- Intracellular or extracellular
- Neurotoxins (anatoxin, saxitoxin)
- Hepatotoxins (microcystin, cylindrospermopsin)
- Suggested guidelines.

Microcystin-LR: 1.0 $\mu\text{g}/\text{L}$

Anatoxin-a: 3 $\mu\text{g}/\text{L}$

Cylindrospermopsin: 1-15 $\mu\text{g}/\text{L}$

Microcystins (hepatotoxins)

Produced by:

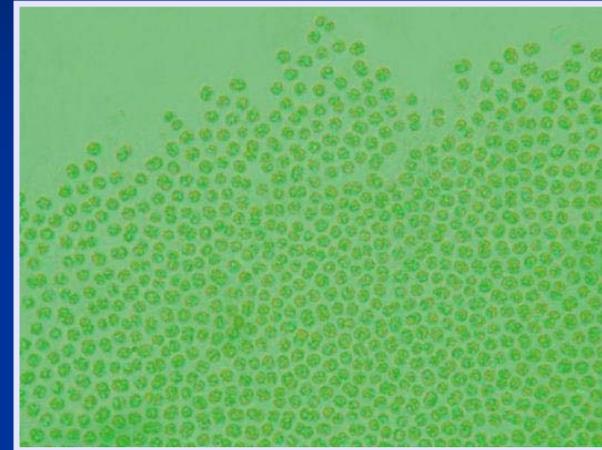
Microcystis,

Anabaena,

Oscillatoria,

Nostoc,

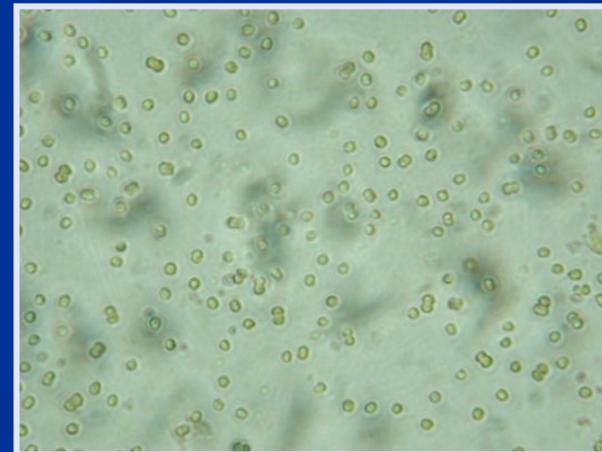
Anabaenopsis



Microcystis aerogenosa



Anabaena flos aquae



Microcystis aerogenosa

Anatoxins (Neurotoxins)

Produced by:

Anabaena,

Oscillatoria,

Aphanizomenon,

Cylindrospermum,

Microcystis



Anabaena sp.



Anabaena variabilis



Anabaena shceremetievi

Microcystin Presence

- Detected in 80% of 677 sources tested in U.S. and Canada (Carmichael, 2001).
- Only 4.3% of source water samples were $>1\mu\text{g}/\text{L}$ in concentration (Carmichael, 2001).



Health Effects?

- Animals
 - Ingestion of Untreated Water

- Humans
 - Direct Contact with Recreational Water
 - Ingestion of Untreated or Poorly Treated Drinking Water



News Release: Avoid swimming in water with mats of blue-green algae

For Release: June 11, 2004

Contact(s): Bob Masnado, DNR, (608) 267-7662
Mark Werner, DHFS, (608) 266-7480

Dane County health officials temporarily closed the beach at Lake Kegonsa State Park Tuesday evening after initial analysis of water samples taken from the beach, other locations on the lake, and a nearby pond indicated high levels of blue-green algae.

DNR water resources staff had collected the samples earlier that day after receiving a call from a woman who reported that her dog suffered seizures after swimming in the pond on private land and in Lake Kegonsa.



Coroner cites algae in teen's death

Experts are uncertain about toxin's role

By DON BEHM

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Last Updated: Sept. 5, 2003

After a yearlong investigation, the Dane County coroner has concluded that the mysterious death of a Cottage Grove teenager last summer likely was the first in the nation caused by exposure to a toxin released by algae.

Two days after swallowing water while splashing and diving in a scum-covered pond at a Dane County golf facility in July 2002, Dane Rogers went into shock and suffered a seizure before his heart failed, according to Coroner John Stanley's report .

Tests of blood and stool samples from both boys found the common blue-green algae, known as *Anabaena flos-aquae*, and its toxin, Anatoxin-a.

Human Risks (other than recreational exposure)

64

Ian R. Falconer*

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Is there a Human Health Hazard from Microcystins in the Drinking Water Supply?*

Microcystins are cyclic heptapeptide toxins produced by a range of cyanobacterial genera. These cyanobacteria occur naturally in drinking water reservoirs subject to eutrophication, and in rivers and natural lakes. Because of the diversity of organisms, the toxins occur from oligo-mesotrophic lakes in North Temperate latitudes, to hypertrophic tropical ponds. The toxins are responsible for numerous cases of injury and death of domestic animals, and human poisoning from drinking water. The initial poisoning includes hepatic cell death. This leads to secondary effects from liver deficiency, including jaundice and photosensitisation. The toxic effects are largely due to inhibition of phosphatase enzymes, acting to regulate protein phosphorylation. The consequences include structural damage, apoptosis and, at lower concentrations, cell cycle effects and tumour promotion. As there is no clear evidence for direct carcinogenesis by microcystins, they are classed as non-carcinogenic toxins in drinking water. Guideline Values for safe drinking water are derived from data for subchronic rodent toxicity, using the No Observed Adverse Effect Level (the highest dose giving no toxicity). To this dose are applied uncertainty factors, to calculate a Tolerable Daily Intake. On the basis of a standard bodyweight and water consumption the Guideline Value is determined for drinking water. For microcystin-LR the WHO have set a provisional Guideline Value of 1 µg/L for drinking water.

Human Fatalities from Cyanobacteria: Chemical and Biological Evidence for Cyanotoxins

Wayne W. Carmichael,¹ Sandra M.F.O. Azevedo,² Ji Si An,¹ Renato J. R. Molica,³ Elise M. Jochimsen,⁴ Sharon Lau,⁵ Kenneth L. Rinehart,⁵ Glen R. Shaw,⁶ and Geoff K. Eaglesham⁷

¹Department of Biological Sciences, Wright State University, Dayton, Ohio, USA; ²Instituto de Biofísica Carlos Chagas Filho, Universidade do Brasil, Rio de Janeiro, Brasil; ³Instituto Tecnológico de Pernambuco, Recife, Brasil; ⁴Hospital Infections Program, National Center for Infectious Diseases, Centers for Disease Control and Prevention, Atlanta, Georgia, USA; ⁵Roger Adams Laboratory, School of Chemical Sciences, University of Illinois, Urbana, Illinois, USA; ⁶National Research Center for Environmental Toxicology, Coopers Plains, Queensland, Australia; ⁷Queensland Health Scientific Services, Coopers Plains, Queensland, Australia

An outbreak of acute liver failure occurred at a dialysis center in Caruaru, Brazil (8°17' S, 35°58' W), 134 km from Recife, the state capital of Pernambuco. At the clinic, 116 (89%) of 131 patients experienced visual disturbances, nausea, and vomiting after routine hemodialysis treatment on 13–20 February 1996. Subsequently, 100 patients developed acute liver failure, and of these 76 died. As of December 1996, 52 of the deaths could be attributed to a common syndrome now called Caruaru syndrome. Examination of phytoplankton from the dialysis clinic's water source,

hypertriglyceridemia; and disruption of liver plates, liver cell deformity, necrosis, apoptosis, cholestasis, cytoplasmic vacuolization, mixed leukocyte infiltration and multinucleated hepatocytes observed upon light microscopy and intracellular edema, mitochondrial changes, rough and smooth endoplasmic retic-

les, and residual body microscopy (5–7). Much attention has been paid to this case and a summary has been published in the past few years. In this paper, we have reviewed the case report of the liver tissue specimens, and address some important issues: these human fatalities: is the reservoir that supplied the dialysis clinic? present, and at what concentrations of the dialysis center high culture and death?

Methods

Isolation and identification. Isolates were not doing identification during

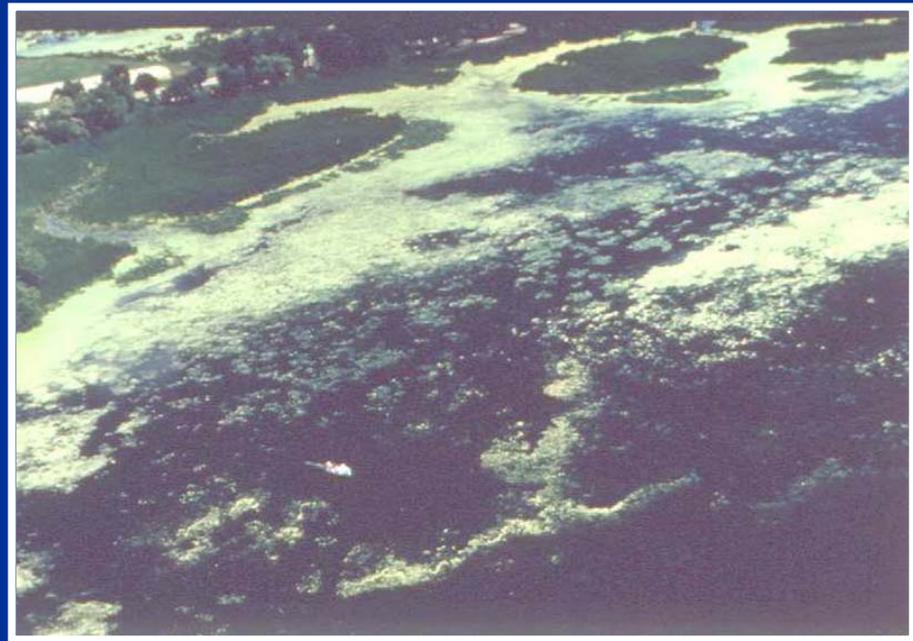
to W.W. Carmichael, Sciences, Wright State University, 3600 Dayton, OH 45435 USA. E-mail: wwc@wright.edu
to confirm ELISA bank C. Holmes, D.M. Cookson, W.R. Jarvis, de M. Filho, and T.M. Immunology, database management, and shipment. An analysis was provided for Disease Control and Prevention (GM 27029), Health (RR 01575), and Liaison (PCM 8121494)

© accepted 30 January

Microcystins in Wisconsin Lakes and Drinking Water Utilities

- In 1998, microcystin algal toxins were found in untreated surface waters in Wisconsin (Karner *et al.*, 2001).
- At times, source concentrations exceeded 1 $\mu\text{g}/\text{L}$.
- The concentrations of toxins increased throughout the summer and into the fall season.
- **The drinking water treatment facilities removed toxins well below the 1 $\mu\text{g}/\text{L}$ guideline.**

Lake Winnebago, WI



There is also good news

Control of Toxic Cyanobacteria Blooms

- Bloom Prevention
- Operational Controls
- Algaecides
- Coagulants



Microcystis sp. bloom



Anabaenopsis sp. bloom

Drinking Water Treatment for Removal of Cyanobacteria Toxins

A) METHODS EFFECTIVE AT REMOVING INTRACELLULAR TOXIN:

- Coagulation-Sedimentation-Filtration:
up to 90% reported removals for intracellular microcystin
- Coagulation- DAF:
40-80% removal of microcystis cells
90-100% removal of anabaena cells



Drinking Water Treatment for Removal of Cyanobacteria Toxins

B) METHODS EFFECTIVE AT REMOVING EXTRACELLULAR TOXIN:

- Powdered Activated Carbon Adsorption:
up to 85% removal of extracellular microcystin
up to 98% removal of extracellular anatoxin
- Granular Activated Carbon:
up to 95% removal of extracellular microcystin and anatoxin



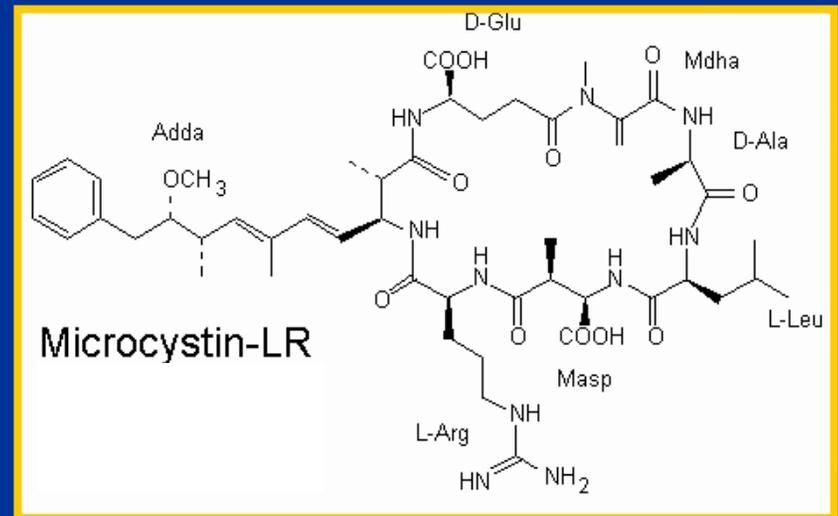
Drinking Water Treatment for Removal of Cyanobacteria Toxins

- Free Chlorine:
up to 100% removal of extracellular microcystin
- Ozone:
up to 100% removal of extracellular microcystin, up to 92% removal of extracellular anatoxin
- Potassium permanganate:
up to 95% removal of microcystin
- Membranes:
up to 95% removal of microcystin with RO membranes



A Chlorination Example

- Chlorination is being used extensively by water utilities in the U.S., and therefore, it can serve as an easily accessible means of microcystin inactivation.
- Microcystin-LR chlorination studies have been performed by Nicholson *et al.*, 1994; Tsuji *et al.*, 1997; Hart *et al.*, 1998; and Bruchet *et al.*, 1998.
- The researchers studied different initial toxin concentrations, chlorine doses, and chlorine to toxin molar ratios.
- The researchers demonstrated that under several conditions the destruction of microcystin with chlorine is possible.



Research Objectives

- ➔ The main objective of the project was to conduct a detailed evaluation of the **inactivation kinetics** of extracellular microcystin-LR by free chlorine at chlorine to microcystin molar ratios representative of water treatment practice (1,500-150,000).
- ➔ The effects of **pH, chlorine dose, microcystin-LR concentration, temperature, and water quality** on the rate of inactivation were evaluated.
- ➔ **CT values** for inactivation of extracellular microcystin-LR by free chlorine were developed (C=residual disinfectant concentration, T= detention time).

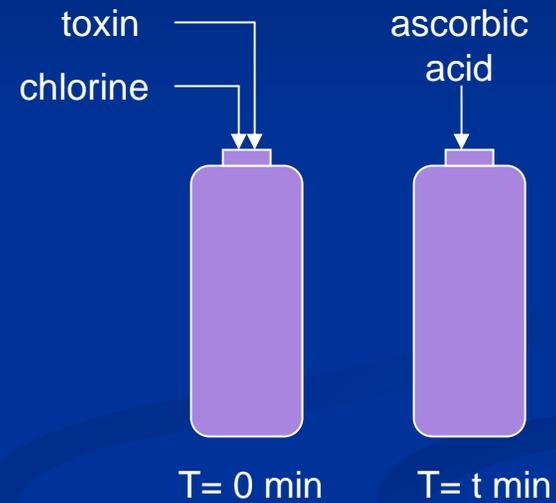
Experimental Design

- Initial Toxin Concentration 1, 3, 10 $\mu\text{g/L}$
- Chlorine Dose 1, 3, 10 mg/L as Cl_2
- pH 6.0, 7.5, 9.0
- Temperature 11°C, 20°C, 29°C
- Contact Time 3, 10, 30, 100 min
- Water buffered MQ, 7 natural waters

Methods

Chlorination tests:

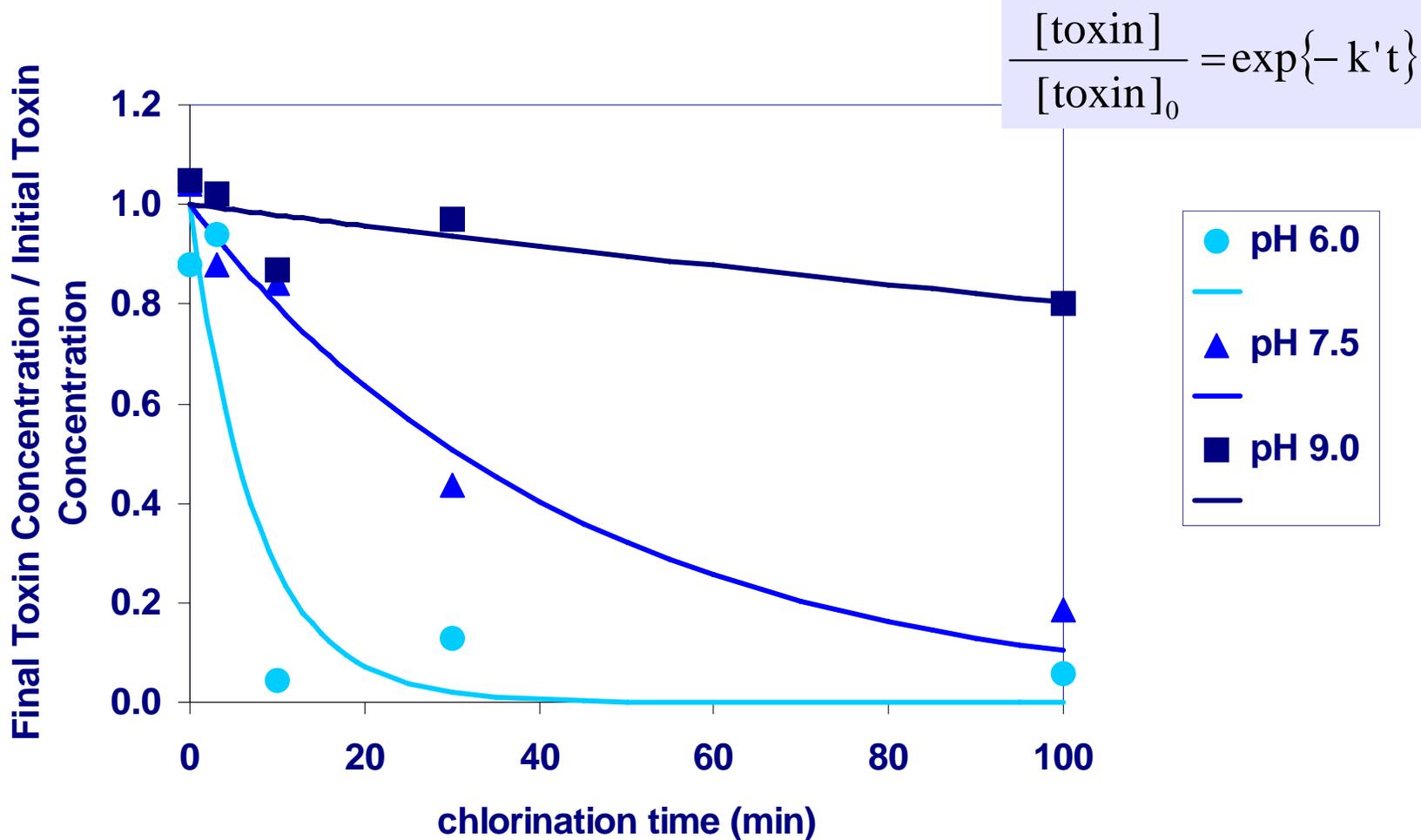
- batch tests conducted in 1L bottles
- toxin added to buffered MQ water
- sodium hypochlorite added
- chlorine residual quenched with ascorbic acid at desired contact time



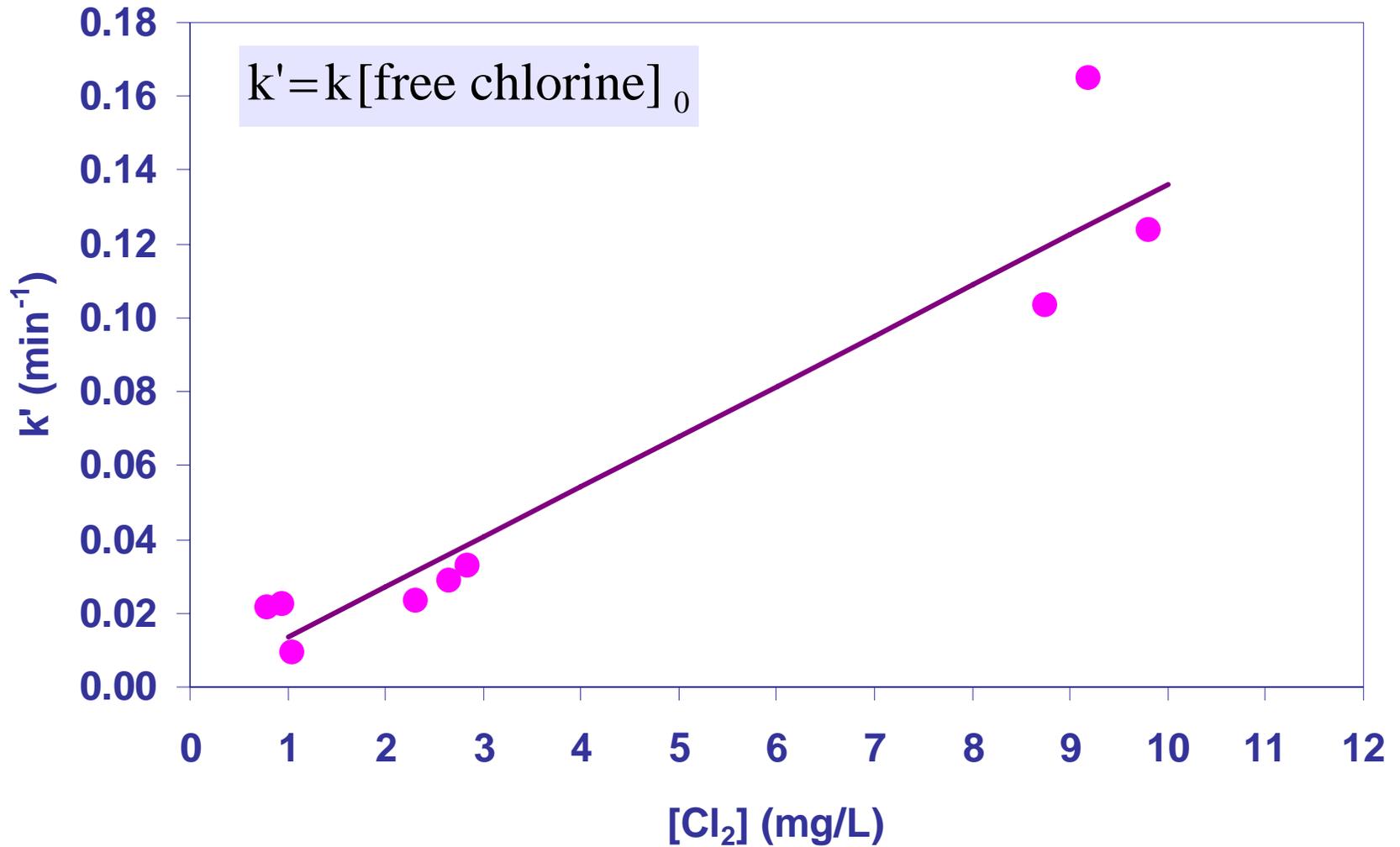
Parameters Measured:

- pH, temperature, chlorine concentration, toxin concentration (measured by ELISA and HPLC)

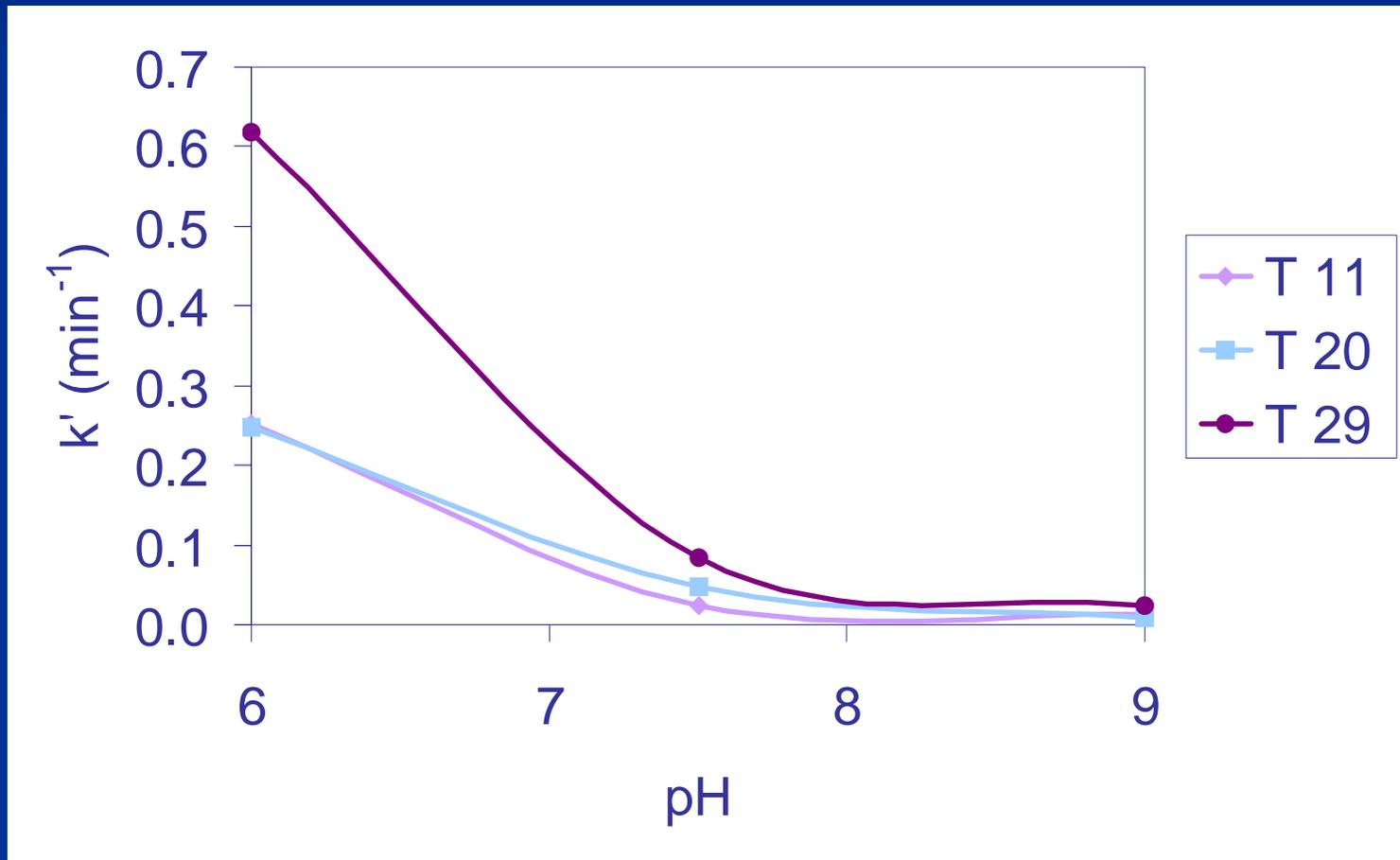
Effect of pH and contact time on microcystin-LR inactivation for 1 mg/L initial toxin concentration and 1 mg/L free chlorine dose



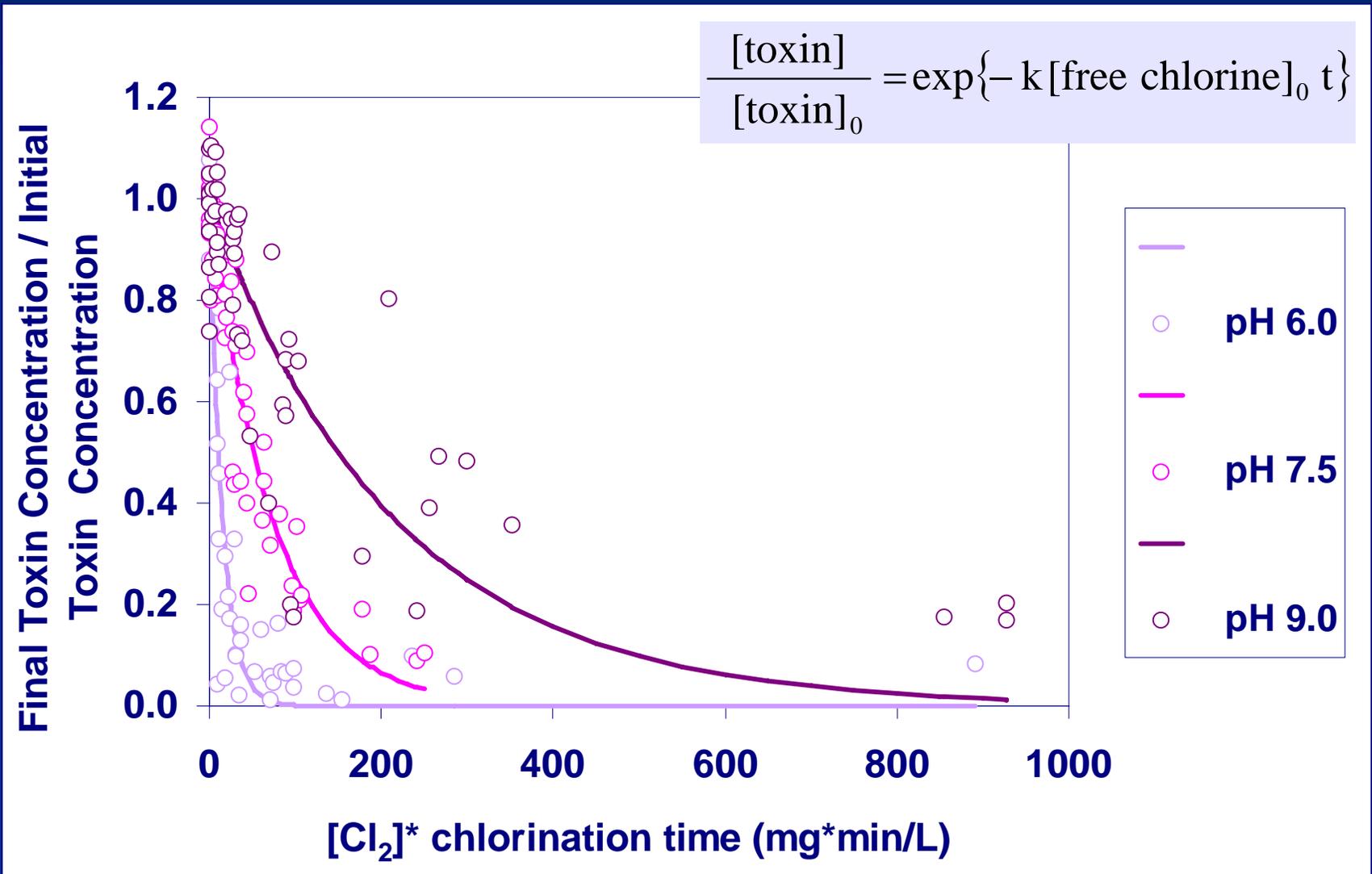
Relationship between inactivation rate constant and chlorine dose at pH 7.5.



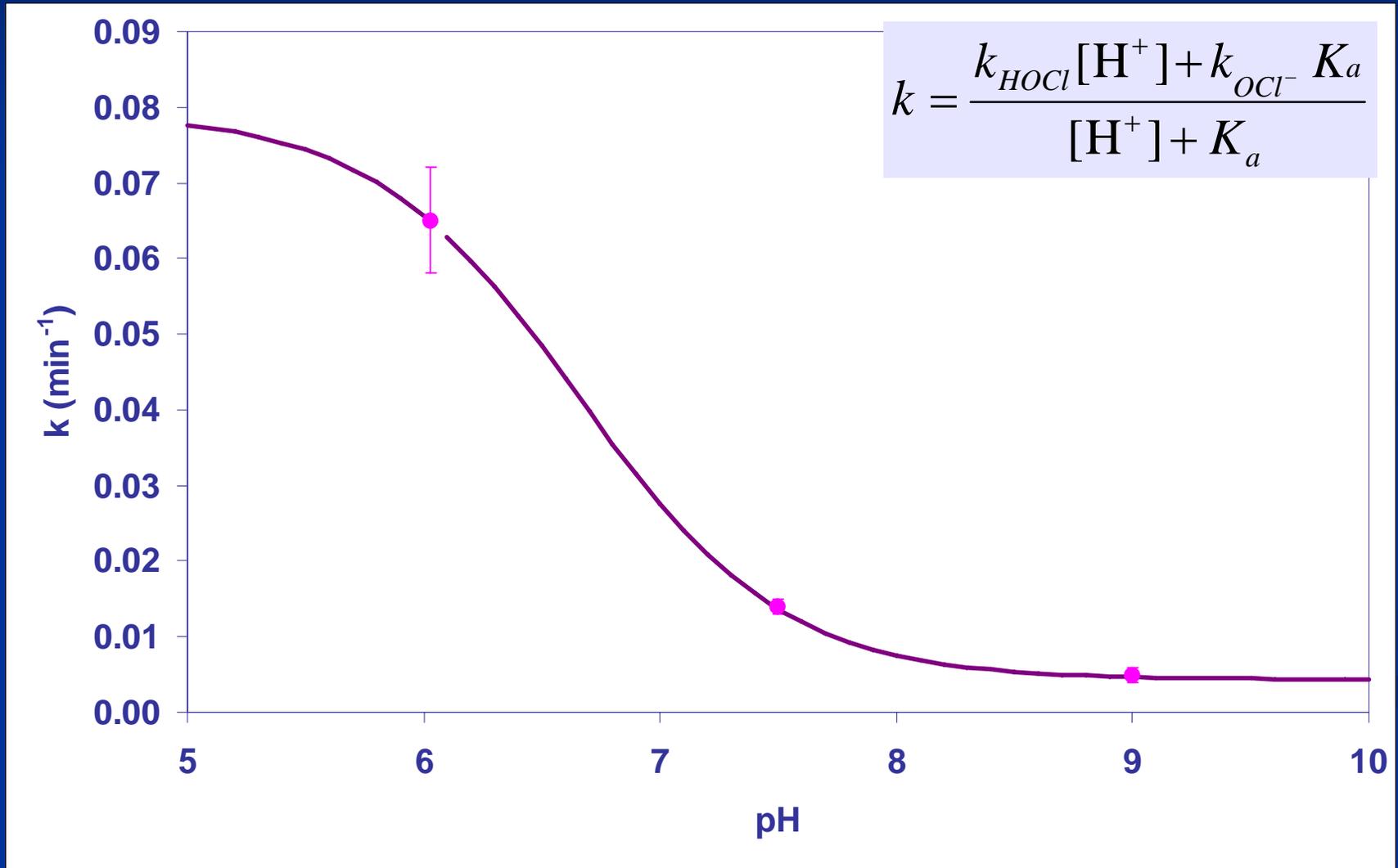
Effect of temperature on inactivation rate constant for 2 $\mu\text{g}/\text{L}$ initial toxin concentration and 1 mg/L free chlorine dose



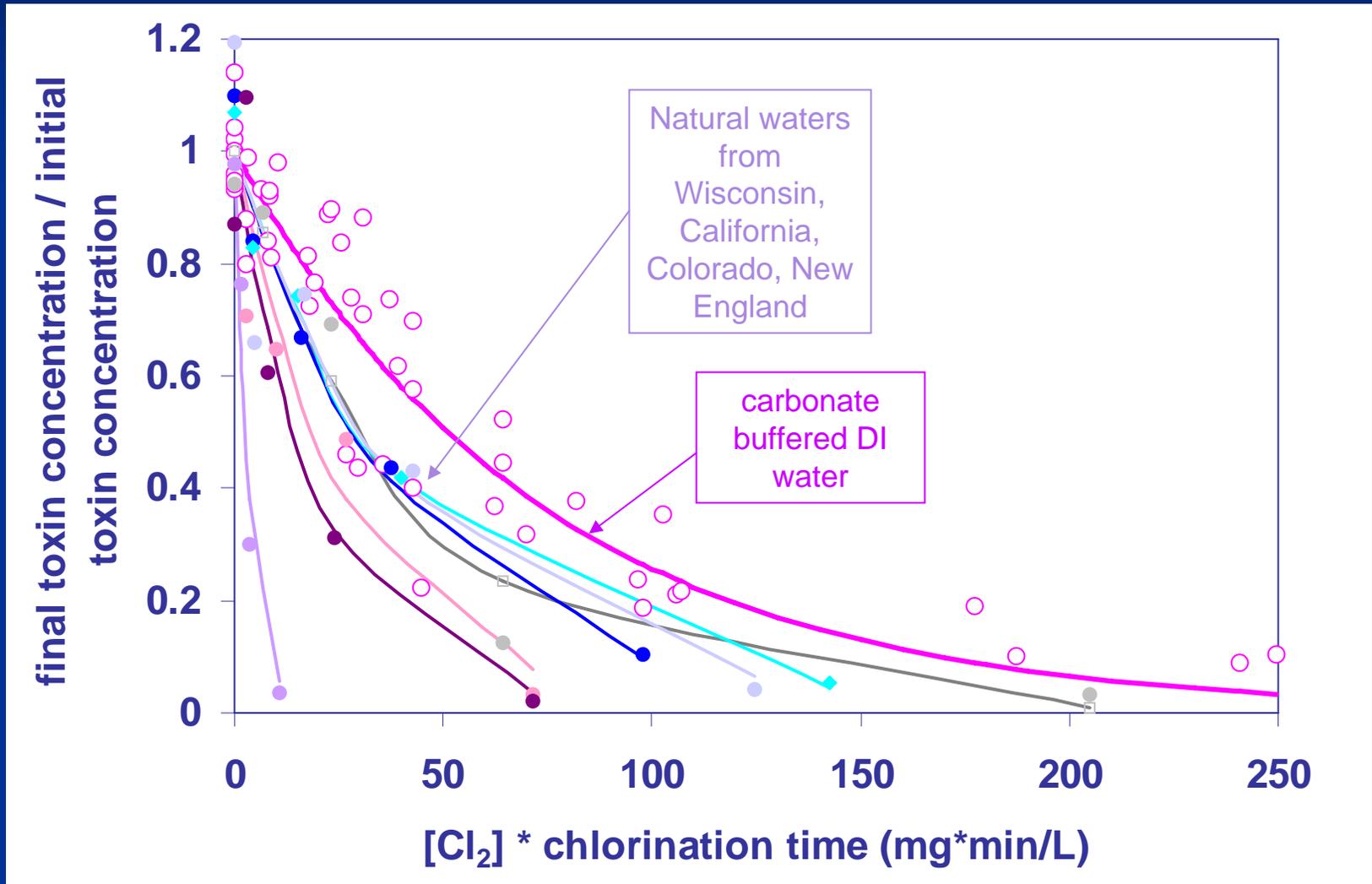
Microcystin-LR inactivation versus CT for three different pH values



Relationship between inactivation rate constant and pH at 11°C and all chlorine doses tested (bars indicate standard errors)



Microcystin-LR inactivation versus CT at pH 7.5 (DI water and 7 natural waters)

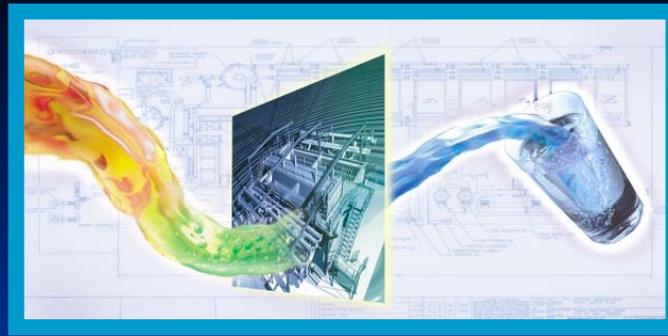


Conclusions

- Extracellular microcystin-LR was effectively inactivated by free chlorine.
- The highest inactivation rates were observed at pH 6.0 and the lowest at pH 9.0.
- At pH 6, 1 log (90%) toxin inactivation was achieved at an average CT of 35 mg*min/L.
- At pH 7.5 and pH 9, 1 log inactivation was achieved at average CT values equal to 169 mg*min/L and 496 mg*min/L respectively.

Recommendations Concerning Drinking Water Exposure

- Source Water Protection
- Early Detection
 - Toxin (chemical measurements)
 - Toxin producing gene (molecular techniques)
 - Indicator parameters
- Bench and Pilot Scale Studies with Natural water



Source water protection
Early Detection
Pilot Tests
Water Treatment

Thank you

For more info: xagorara@msu.edu

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