

Reduction of extracellular microcystin by an advanced oxidation technique: potential of boron-doped electrodes to control cyanobacterial blooms

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Cyanobacteria



Lake Bled, Slovenia
(Credit: M. Čater, Arhel Ltd.)



Pond in Hotinja vas, Slovenia
(Credit: M. Čater, Arhel Ltd.)



Lake Taihu, China
(Credit: H. Paerl, University of North Carolina)



Planktothrix rubescens and *Microcystis aereginosa*

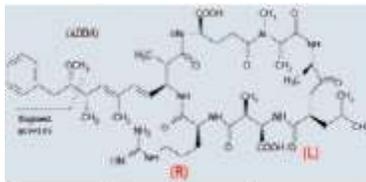
Microcystins



- cyclic peptides, belonging to the family of cyanotoxins
- produced by different cyanobacterial genera (*Microcystis*, *Anabaena*, *Planktothrix*, *Nostoc*, *Haplasiphon* and *Anabaenopsis*)
- *hepatotoxic, neurotoxic, genotoxic*
- synthesized at late logarithmic phase of growth
- released in smaller proportions during proliferation but in greater quantity during the ageing and lysis of the bloom

Microcystin-LR

- *Planktothrix rubescens* is known to produce microcystin-RR



MC Variants	R	L
MC-LR	Leucine	Arginine
MC-RR	Arginine	Arginine
MC-YR	Tyrosine	Arginine

Source: AZO Materials, Analysis of Microcystins in Drinking Water Using LC-MS/MS, 2012

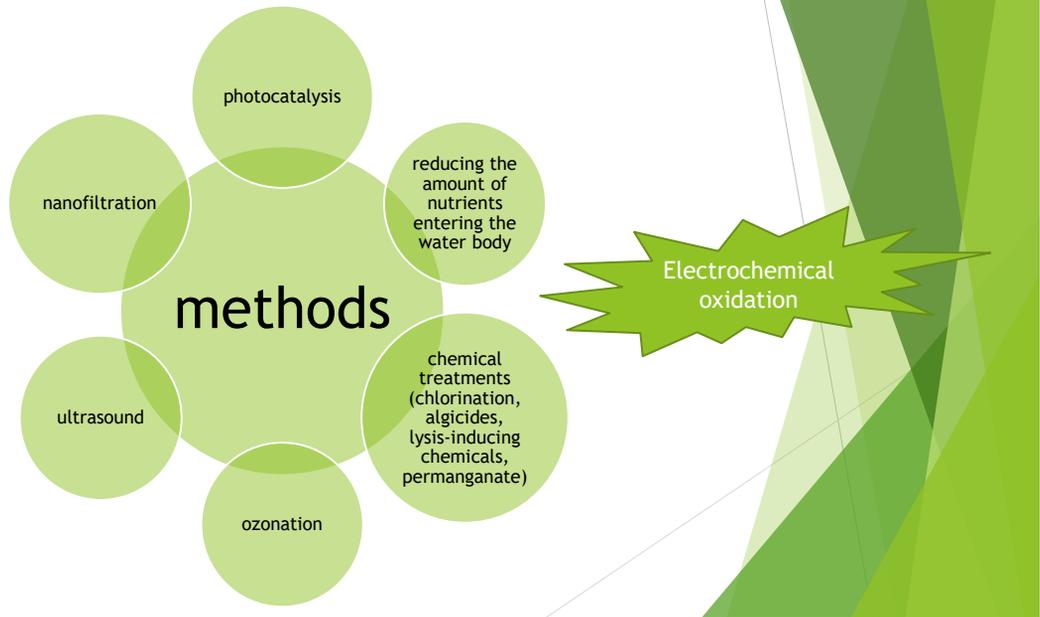
Planktothrix rubescens

- ▶ a filamentous cyanobacterium
- ▶ found in middle European and Southern sub-alpine lakes
- ▶ some clones produce microcystins
- ▶ their massive blooms are a sign of a destroyed equilibrium in the lake (too high nutrient concentration in the water body)



Lake Bled, Slovenia:
1.45 km²
25,700 ML
maximum depth of 30 m

Preventing cyanobacterial blooms

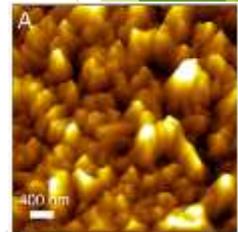


Electrochemistry for the environment

- ▶ Electrochemical oxidation: a perspective method in development
- ▶ Reduction of cyanobacteria quantity and microcystin concentration
- ▶ Formation of **hydroxyl radicals**, ozone, peroxide and other oxygen compounds directly from water due to the electric power
- ▶ Hydroxyl radicals unselectively react with organic compounds
- ▶ Half-life of hydroxyl radicals is 10^{-9} s \rightarrow no hazard in the outflow



- ▶ Microcystin degradation depends on treatment time, current density and electrolytes concentration dissolved in water
- ▶ **Boron-doped diamond (BDD) electrodes** (inertness, durability, radicals)



Atomic force microscopy of BDD electrode surface
(source: Enache et al., 2009)

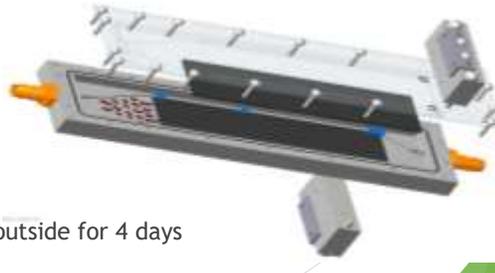
Materials and methods

- ▶ the effect of electro-chemical oxidation on the quantity and viability of *P. rubescens* and on concentration of extracellular microcystins was examined
- ▶ Fresh lake water sample was collected at Lake Bled, Slovenia



- ▶ Treated water samples were pumped through an active BDD electrolytic cell

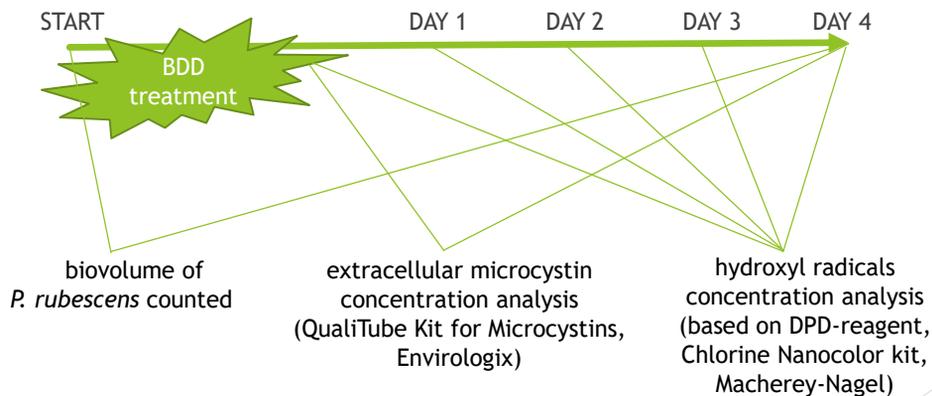
50 mA/cm² current density
1 L/min flow rate
0.72 s electro-oxidation time



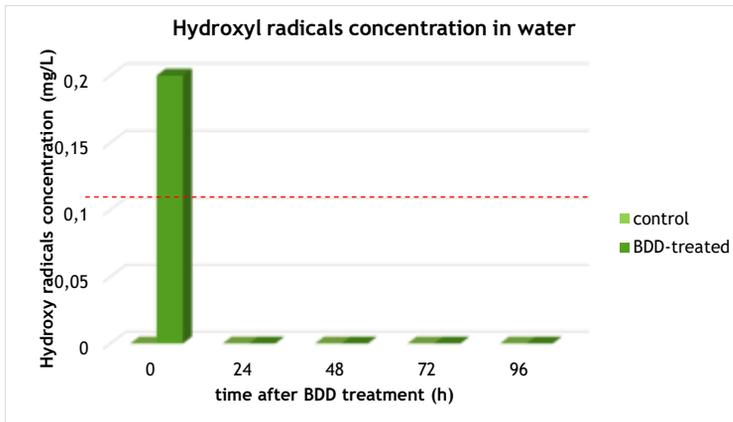
- ▶ 4 L tanks in batch mode, placed outside for 4 days



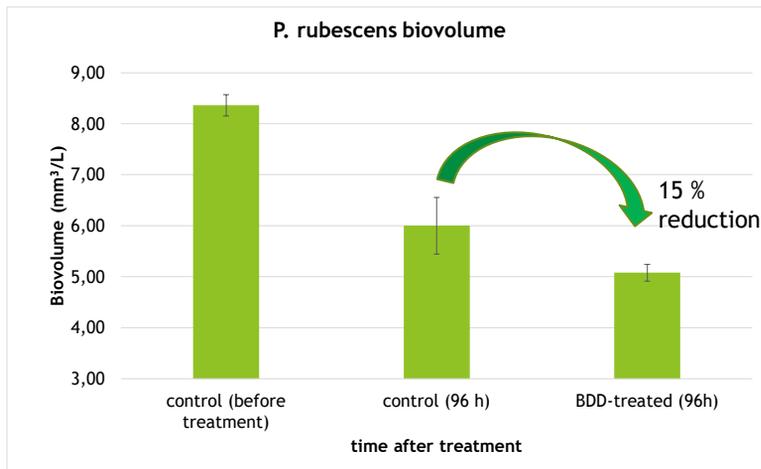
Materials and methods



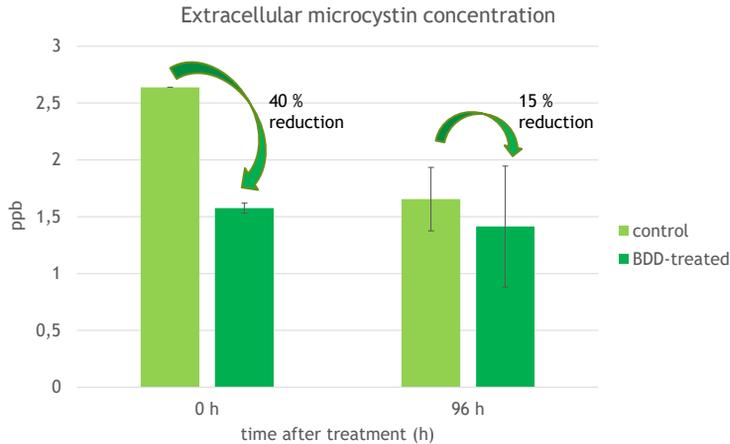
Short-living hydroxyl radicals



Reduced quantity of *P. rubescens*



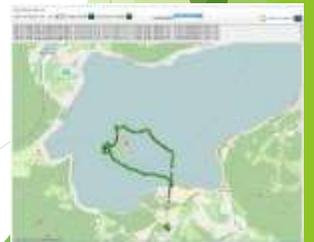
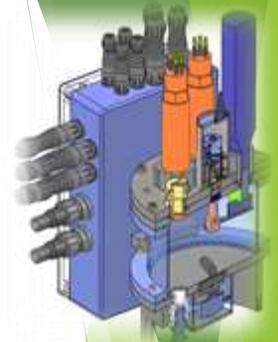
Instant extracellular microcystin concentration drop



Robotic floating platform for control of cyanobacteria



- ▶ Solar powered
- ▶ Early warning system: automated online real-time monitoring of cyanobacterial and algal quantity using fluorescence phycocyanin and chlorophyll sensors
- ▶ Control of cyanobacterial growth: double BDD electrodes
- ▶ Navigation, automated docking system, autonomous decision-making system, real-time transfer of measurements to the server and on the web page
- ▶ Suitable for lakes and drinking water reservoirs



ARHEL team



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