Supplementary information

Title: Exploring the Dynamics of Reactive Oxygen Species from CaviPlasma and their Disinfection and Degradation Potential – the case of cyanobacteria and cyanotoxins

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LC-MS/MS analysis of microcystins

A Poroshell 120 EC-C18 column (2.1 x 100 mm; 2.7 μm) with a matching safety guard column (Agilent Technologies, CA, USA) was used for separation. Mobile phases A and B consisted of 0.1% formic acid in water and acetonitrile, respectively. The gradient elution was used for separation with increasing amounts of B fraction from 5 % to 55 % within 5 minutes and then to 90 % within 3 minutes, followed by a 4-minute hold. The flow rate was established at 200 μL min^{-1}, column temperature 45°C and the injection volume was set at 10 μL. The detector settings were configured as follows: capillary voltage at 4500 V, nozzle voltage at 500 V, gas temperature (N_2) at 350°C, gas flow at 10 mL min^{-1}, nebuliser at 20 psi, sheath gas temperature (N_2) at 350°C, and sheath gas flow at 12 mL min^{-1}. Mass data collection was performed using MassHunter Workstation software (Agilent Technologies, CA, USA) via multiple reaction monitoring (MRM) in positive mode. Transitions of individual MCs are listed in Table S1.

Table S1 Transitions of individual MCs

Compound	CAS Number	Retention time (min)	Precursor ion (m/z)	Product ion[a] (m/z)	Fragmentor (V)	CE[b] (eV)
MC-RR	111755-37-4	8.87	520	135/213	140	30/35
MC-YR	101064-48-6	9.39	523	135/70	90	50
MC-LR	101043-37-2	9.57	498	135/213	90	13/29
MC-WR	138234-58-9	9.68	535	135/103	100	13/69
MC-LA	96180-79-9	10.57	911	135/213	170	75/50
MC-LY	123304-10-9	10.60	1003	135/213	200	50/75
MC-LW	157622-02-1	10.97	1026	135/213	200	80/53
MC-LF	154037-70-4	11.18	987	135/213	170	78/68

[a] quantifier/qualifier, [b] collision energy

Solid phase extraction of microcystins

The SPE Oasis® HLB (500 mg, 6 mL) cartridges (Waters, Milford, MA) were conditioned using 5 mL of methanol followed by 5 mL of Milli-Q water. A portion of 50 mL of samples (pH = 5 - 6) was extracted under vacuum at a flow rate of approximately 5 mL min^{-1}. Afterwards, the sample holders were rinsed with 5 mL of distilled water and dried under vacuum suction for 20 min. Once extraction was completed, analytes were eluted with 5 mL of methanol and dried under a gentle nitrogen stream at 45°C. The dried extract was reconstituted in methanol/water (1:1, v/v) before LC-MS/MS analysis.

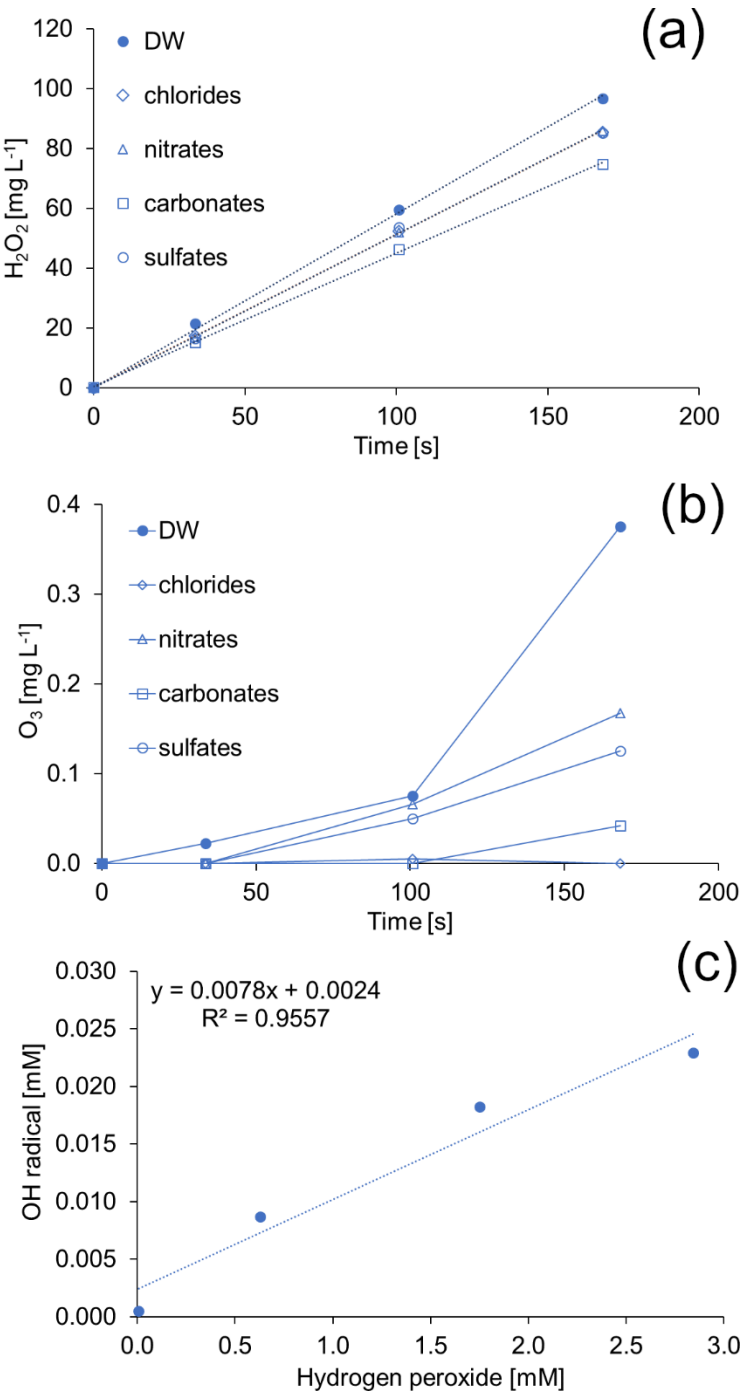

Fig. S1 Changes in the levels of hydrogen peroxide (a) and ozone (b) content as a function of treatment time in the presence of sodium salts. A four-litre batch was used in this experiment. Correlation of hydrogen peroxide and hydroxyl radical content in deionised water (c). Treatment times correspond to SIE of 8.4 kJ L^{-1}, 25.2 kJ L^{-1}, and 42 kJ L^{-1}

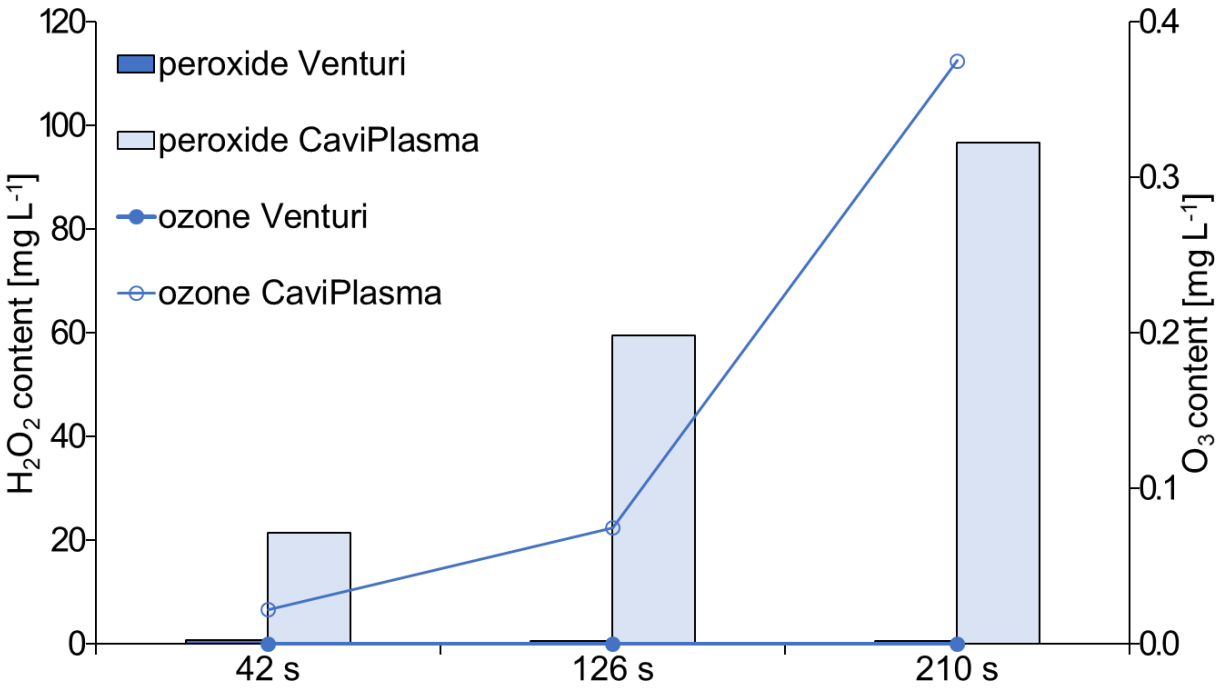

Fig. S2 The effect of sole-cavitation (Venturi) and synergistic action of discharge and cavitation (CaviPlasma) on hydrogen peroxide and ozone content

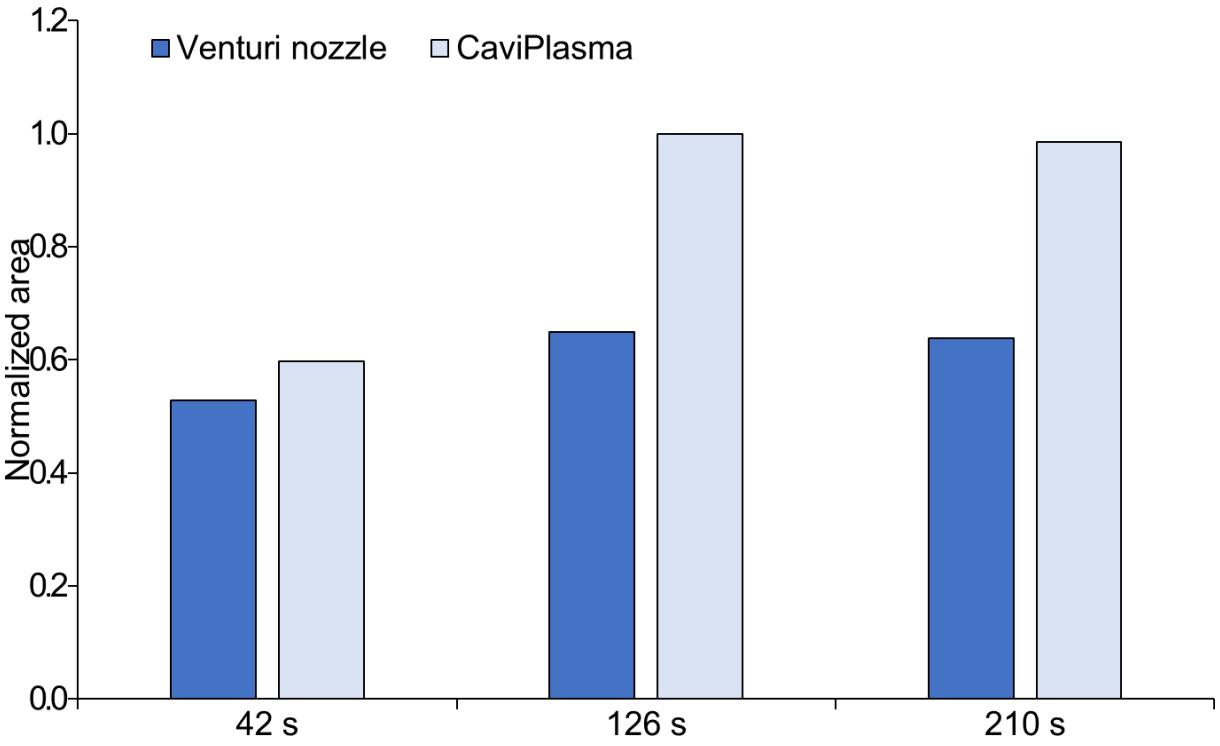

Fig. S3 The effect of sole-cavitation (Venturi) and synergistic action of discharge and cavitation (CaviPlasma) on yield of hydroxyl radicals

Composition of ZBB medium

Medium Z and BB were mixed in a 1:1 ratio (v/v) and diluted to 25%. The medium's conductivity and pH were 273.1 μS cm^{-1} and 7.0, respectively.

Medium Z	**c [mg L^{-1}]**
$NaNO_3$	467
$Ca(NO_3)_2 . 6H_2O$	59
K_2HPO_4	31
$MgSO_4 . 7H_2O$	25
Na_2CO_3	21
$NiSO_4(NH_4)_2SO_4 .6H_2O$	$1.6x10^{-2}$
$V_2O_4(SO_4)_3 . 16H_2O$	$2.5x10^{-3}$
$(NH_4)_6 Mo_7O_{24} . 4H_2O$	$7.0x10^{-3}$
$ZnSO_4 . 7H_2O$	$2.3x10^{-2}$
$Cd(NO_3)_2 .4H_2O$	$1.2x10^{-2}$
$Al_2(SO_4)_3K_2SO_4 . 24H_2O$	$3.8x10^{-2}$
$Na_2WO_4 . 2H_2O$	$2.6x10^{-3}$
KBr	$9.5x10^{-3}$
H_3BO_3	$2.5x10^{-2}$
$MnSO_4 . 4H_2O$	$1.8x10^{-1}$
$Cr(NO_3)_3 . 7H_2O$	$1.2x10^{-2}$
KI	$6.6x10^{-3}$
$CuSO_4 . 5H_2O$	$1.0x10^{-2}$
$FeCl_3$	2.8
Chelaton III	3.7
0.1N HCl	0.2 ml

Medium BB	**c [mg L^{-1}]**
$NaNO_3$	250
$CaCl_2 . 2H_2O$	25
K_2HPO_4	75
KH_2PO_5	175
$MgSO_4 . 7H_2O$	75
NaCl	25
Chelaton III	50
KOH	31
$FeSO_4 .7H_2O$	5.0
H_2SO_4 (conc.)	0.1
H_3BO_3	11.4
$MnCl_2 . 4H_2O$	1.4
$CuSO_4 . 5H_2O$	1.6
MoO_3	0.7
$ZnSO_4 . 7H_2O$	8.8
$Co(NO_3)_2 . 6H_2O$	0.5

Table S2 The concentration of individual microcystins in spiked water (determined by LC-MS/MS) for MC's removal experiment. The data expressed as average values ± standard deviation (n=4)

Fortified water	**MC_RR**	**MC_YR**	**MC_LR**	**MC_LY**	**MC_LW**	**MC_LF**
Concentration [µg L^{-1}]	0.67 ± 0.03	0.14 ± 0.02	2.46 ± 0.19	0.09 ± 0.01	0.16 ± 0.02	0.19 ± 0.01

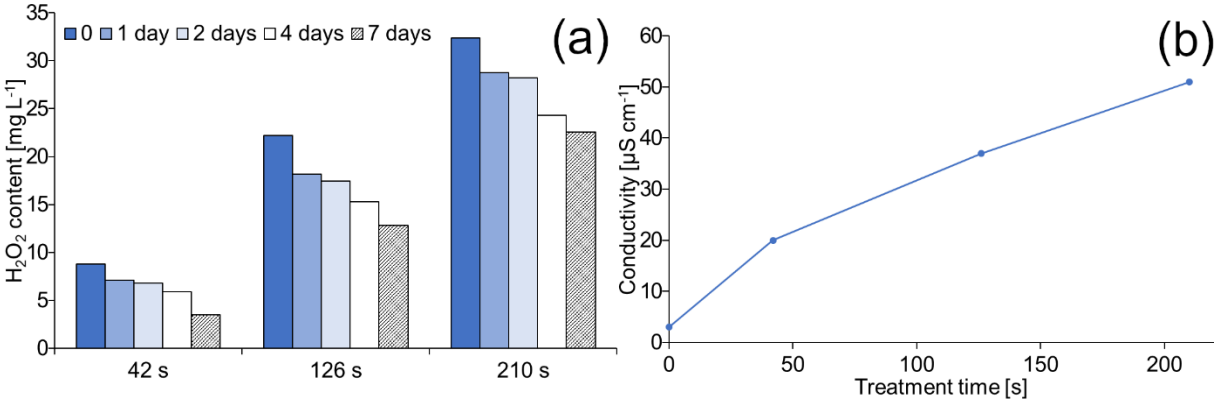

Fig. S4 Changes of hydrogen peroxide concentration (a) after treatment and conductivity with treatment time (b) in deionised water spiked with MC