Supplementary Information

Untargeted LC-HRMS applied to microcystin-producing cyanobacterial cultures for the evaluation of the efficiency of chlorine-based treatments commonly used for water potabilization

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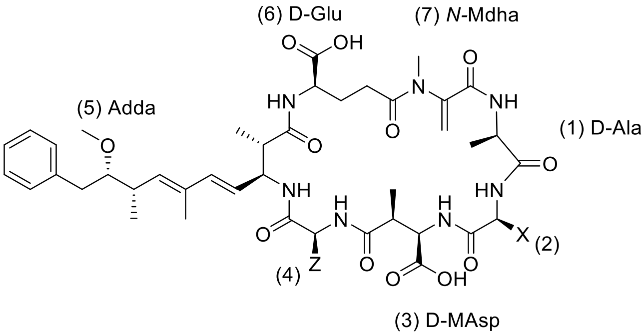
Table S1. Chemical structures of microcystins (MCs) and their dihydroxy and/or monochloro-hydroxy products formed through reaction with chlorine at the conjugated double bonds of Adda residue. X and Z represent variable L-amino acids at position-2 and -4. Exact masses, elemental compositions (for $[M+H]^+$ ions) and retention times of MC variants and their degradation products detected in the cyanobacterial intracellular and extracellular fractions.



Microcystin (MC-XZ)	**$[M+H]^+$, *m/z***	**Rt (min)**	**Elemental Formula**
MC-LR	995.5571	15.9	$C_{49}H_{75}O_{12}N_{10}^+$
[Dha^7]MC-LR	981.5412	16.0	$C_{48}H_{73}O_{12}N_{10}^+$
MC-LF	986.5250	16.2	$C_{52}H_{72}O_{12}N_7^+$
[D-Asp^3]MC-LF	972.5087	16.1	$C_{51}H_{70}O_{12}N_7^+$
MC-LY	1002.5197	15.4	$C_{52}H_{72}O_{13}N_7^+$
[D-Asp^3]MC-LY	988.5045	15.2	$C_{51}H_{70}O_{13}N_7^+$
Dihydroxy-MC-LR	1029.5542	13.4	$C_{49}H_{77}O_{14}N_{10}^+$
Monochloro-hydroxy-MC-LR	1047.5265	14.3	$C_{49}H_{76}ClO_{13}N_{10}^+$
Dihydroxy-[Dha^7]MC-LR	1015.5459	17.0	$C_{48}H_{75}O_{14}N_{10}^+$
Monochloro-hydroxy-[Dha^7]MC-LR	1033.5077	14.6	$C_{48}H_{74}ClO_{13}N_{10}^+$
Dihydroxy-MC-LF	1020.5288	14.7	$C_{52}H_{74}O_{14}N_7^+$
Monochloro-hydroxy-MC-LF	1038.4949	12.3	$C_{52}H_{73}ClO_{13}N_7^+$
Dihydroxy-[D-Asp^3]MC-LF	1006.5132	14.9	$C_{51}H_{72}O_{14}N_7^+$
Monochloro-hydroxy-[D-Asp^3]MC-LF	1024.4793	11.2	$C_{51}H_{71}ClO_{13}N_7^+$
Monochloro-hydroxy-MC-LY	1054.4899	11.3	$C_{52}H_{73}ClO_{14}N_7^+$
Dihydroxy-[D-Asp^3]MC-LY	1022.5081	14.6	$C_{51}H_{72}O_{15}N_7^+$
Monochloro-hydroxy-[D-Asp^3]MC-LY	1040.4742	11.2	$C_{51}H_{71}ClO_{14}N_7^+$

Table S2. EC_{50} values of NaClO and ClO_2 leading to a 50% inhibition of *M. aeruginosa* photosynthetic efficiency. Calculations are based on photosynthetic efficiency parameters of photosystem II (PSII), i.e., maximum quantum yield (ΦPSII) and effective quantum yield (Φ'PSII). The corresponding EC_{50} dose-response curve are reported in Fig. S1

	NaClO		ClO_2	
Time exposure	EC_{50} (ΦPSII)	EC_{50} (Φ'PSII)	EC_{50} (ΦPSII)	EC_{50} (Φ'PSII)
1 h	0.28±0.01	0.29±0.02	0.53±0.03	0.52±0.04
24 h	0.33±0.03	0.34±0.02	0.59±0.04	0.50±0.05

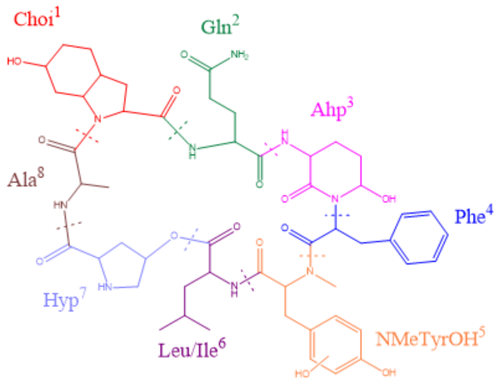
Table S3. Main effects observed on cyanobacterial cells after the application of oxidant treatments. $\Delta Tox(\%)_{TOT}$ = percent removal of total toxins (intracellular plus extracellular) based on toxin concentration per volume (µg L^{-1}) and per cell (pg $cell^{-1}$); cell decrease (%/ctrl) = percent removal of cells; cell ratio (treat/ctrl) = ratio between the number of cells after each treatment and the mean of cell counts in controls; ΦPSII (%) = percent inhibition of the maximum quantum yield; Φ'PSII (%) = percent inhibition of the effective quantum yield

Treatment	Oxidant dose (mg L^{-1})	Treatment time (h)	$\Delta Tox(\%)_{TOT}$ per volume	$\Delta Tox(\%)_{TOT}$ per cell	Cell decrease (%/ctrl)	Cell ratio (treat/ctrl)	ΦPSII (%)	Φ'PSII (%)
NaClO	0.5	1	0.95±18.24	7.88±20.06	-8.37±3.81	1.08±0.04	4.1±4.6	0.0
	0.5	3	-15.67±14.80	-9.66±19.66	-6.87±5.77	1.07±0.06	5.5±4.8	0.0
ClO_2	0.5	1	20.20±25.14	-11.07±43.03	32.79±21.13	0.67±0.21	16.6±2.0	2.6±3.0
	0.5	3	25.80±4.18	-14.05±8.97	36.66±3.43	0.63±0.03	10.9±3.9	5.2±9.0
	2.0	1	57.64±3.60	21.79±8.91	45.69±6.16	0.54±0.06	23.1±4.5	0.0±0.0
	2.0	3	56.30±6.08	18.73±12.94	46.08±5.38	0.54±0.05	15.7±8.4	1.3±2.2

Table S4. Concentration of toxin congeners before and after the oxidation experiment expressed as volume (μg L^{-1}) and per cell (pg $cell^{-1}$). Toxin extraction efficiency from biomass and water was considered 100%, based on data reported in Materials and Methods section 2.7.1. CPtp = cyanopeptolin-type peptides (-1029 and -1045)

	Treatment	MC-LR		[Dha^7]MC-LR		MC-LF		[D-Asp^3]MC-LF		MC-LY		[D-Asp^3]MC-LY		CPtp-1029		CPtp-1045		TOT.	
		μg L^{-1}	pg $cell^{-1}$	μg L^{-1}	pg $cell^{-1}$	μg L^{-1}	pg $cell^{-1}$	μg L^{-1}	pg $cell^{-1}$	μg L^{-1}	pg $cell^{-1}$	μg L^{-1}	pg $cell^{-1}$	μg L^{-1}	pg $cell^{-1}$	μg L^{-1}	pg $cell^{-1}$	μg L^{-1}	pg $cell^{-1}$
Intracellular	CTRL	20.423 ± 0.706	0.1693 ± 0.0097	6.436 ± 0.326	0.0533 ± 0.0029	1.323 ± 0.128	0.011 ± 0.0015	0.077 ± 0.037	0.0006 ± 0.0003	1.448 ± 0.058	0.012 ± 0.001	0.458 ± 0.02	0.0038 ± 0.0003	81.124 ± 4.141	0.673 ± 0.0533	2.272 ± 0.507	0.019 ± 0.0051	113.561 ± 5.655	0.9421 ± 0.074
	NaClO (0.5) 1h	1.084 ± 0.095	0.0083 ± 0.0004	0.128 ± 0.023	0.001 ± 0.0002	0.348 ± 0.058	0.0026 ± 0.0003	0.076 ± 0.016	0.0006 ± 0.0001	0.261 ± 0.028	0.002 ± 0.0002	0.06 ± 0.007	0.0005 ± 0	6.567 ± 0.485	0.0501 ± 0.002	0.014 ± 0.005	0.0001 ± 0	8.538 ± 0.681	0.0651 ± 0.0029
	NaClO (0.5) 3h	1.15 ± 0.727	0.0091 ± 0.0062	0.29 ± 0.08	0.0022 ± 0.0006	0.331 ± 0.068	0.0026 ± 0.0006	0.063 ± 0.022	0.0005 ± 0.0002	0.27 ± 0.073	0.0021 ± 0.0007	0.071 ± 0.018	0.0006 ± 0.0002	5.652 ± 3.427	0.0446 ± 0.0294	<LOD	<LOD	7.827 ± 4.38	0.0617 ± 0.0377
	ClO_2 (0.5) 1h	0.269 ± 0.012	0.0035 ± 0.0011	0.112 ± 0.004	0.0015 ± 0.0004	0.081 ± 0.01	0.001 ± 0.0003	0.016 ± 0.001	0.0002 ± 0.0001	0.028 ± 0.004	0.0004 ± 0.0001	<LOD	<LOD	0.36 ± 0.119	0.0046 ± 0.0017	0.075 ± 0.015	0.0009 ± 0.0001	0.941 ± 0.117	0.0121 ± 0.0028
	ClO_2 (0.5) 3h	0.246 ± 0.043	0.0032 ± 0.0004	0.106 ± 0.011	0.0014 ± 0.0001	0.06 ± 0.008	0.0008 ± 0.0001	0.006 ± 0.005	0.0001 ± 0.0001	0.018 ± 0.009	0.0002 ± 0.0001	<LOD	<LOD	0.412 ± 0.315	0.0053 ± 0.0039	0.139 ± 0.02	0.0018 ± 0.0004	0.987 ± 0.369	0.0128 ± 0.0044
	ClO_2 (2.0) 1h	0.321 ± 0.046	0.0049 ± 0.0006	0.121 ± 0.014	0.0019 ± 0.0003	0.069 ± 0.013	0.001 ± 0.0001	0.003 ± 0.005	0 ± 0.0001	0.018 ± 0.007	0.0003 ± 0.0001	<LOD	<LOD	0.321 ± 0.108	0.005 ± 0.0021	0.048 ± 0.006	0.0007 ± 0.0001	0.902 ± 0.139	0.0139 ± 0.0027
	ClO_2 (2.0) 3h	0.261 ± 0.063	0.0041 ± 0.0014	0.114 ± 0.047	0.0018 ± 0.0009	0.05 ± 0.006	0.0008 ± 0.0002	0.003 ± 0.006	0.0001 ± 0.0001	0.005 ± 0.005	0.0001 ± 0.0001	<LOD	<LOD	0.242 ± 0.053	0.0037 ± 0.0005	0.027 ± 0.004	0.0004 ± 0.0001	0.703 ± 0.072	0.0109 ± 0.0021
Extracellular	CTRL	69.566 ± 3.497	0.5779 ± 0.0593	49.518 ± 2.435	0.4109 ± 0.0334	2.391 ± 0.552	0.02 ± 0.0056	1.767 ± 0.577	0.0148 ± 0.0056	0.971 ± 0.465	0.0081 ± 0.0041	0.853 ± 0.969	0.007 ± 0.0077	2.123 ± 1.217	0.0175 ± 0.0096	0.151 ± 0.134	0.0013 ± 0.0012	127.34 ± 8.899	1.0575 ± 0.1144
	NaClO (0.5) 1h	89.265 ± 2.083	0.6825 ± 0.037	55.239 ± 0.481	0.4221 ± 0.014	3.813 ± 0.11	0.0291 ± 0.001	2.467 ± 0.032	0.0189 ± 0.0006	2.177 ± 0.95	0.0168 ± 0.0077	0.795 ± 0.642	0.0062 ± 0.005	73.692 ± 47.772	0.5715 ± 0.3772	4.253 ± 5.109	0.0317 ± 0.0373	231.702 ± 46.021	1.7788 ± 0.4054
	NaClO (0.5) 3h	99.203 ± 15.414	0.7732 ± 0.1529	60.636 ± 9.341	0.4727 ± 0.0944	4.503 ± 0.778	0.0351 ± 0.0074	2.926 ± 0.686	0.0229 ± 0.0063	2.99 ± 1.181	0.0235 ± 0.0102	0.9 ± 1.221	0.0073 ± 0.0101	106.636 ± 18.597	0.8324 ± 0.1872	5.55 ± 2.75	0.0425 ± 0.0203	283.344 ± 45.378	2.2095 ± 0.4548
	ClO_2 (0.5) 1h	90.198 ± 9.853	1.2056 ± 0.469	56.027 ± 5.54	0.7478 ± 0.2822	3.589 ± 0.725	0.0487 ± 0.0231	2.074 ± 0.529	0.0284 ± 0.0149	0.68 ± 0.997	0.011 ± 0.0169	0.317 ± 0.549	0.0053 ± 0.0092	31.382 ± 51.164	0.5163 ± 0.8588	7.68 ± 6.418	0.0885 ± 0.0792	191.947 ± 61.792	2.6515 ± 1.5569
	ClO_2 (0.5) 3h	86.799 ± 1.669	1.1371 ± 0.0843	54.214 ± 1.477	0.7102 ± 0.0541	3.719 ± 0.25	0.0486 ± 0.0008	2.361 ± 0.152	0.031 ± 0.0037	0.143 ± 0.049	0.0019 ± 0.0008	<LOD	<LOD	3.941 ± 2.728	0.0514 ± 0.0342	26.583 ± 7.913	0.3514 ± 0.1233	177.761 ± 10.066	2.3314 ± 0.2574
	ClO_2 (2.0) 1h	52.419 ± 4.185	0.8042 ± 0.0984	35.283 ± 2.877	0.5408 ± 0.0611	2.063 ± 0.396	0.0314 ± 0.0039	1.241 ± 0.428	0.0186 ± 0.0044	<LOD	<LOD	<LOD	<LOD	0.181 ± 0.11	0.0028 ± 0.0019	9.955 ± 0.847	0.1523 ± 0.0132	101.142 ± 8.538	1.5501 ± 0.1754
	ClO_2 (2.0) 3h	55.145 ± 7.156	0.8514 ± 0.132	36.369 ± 5.337	0.5609 ± 0.0882	2.097 ± 0.571	0.0323 ± 0.0086	1.168 ± 0.542	0.018 ± 0.0081	<LOD	<LOD	<LOD	<LOD	0.092 ± 0.018	0.0014 ± 0.0003	9.704 ± 1.005	0.15 ± 0.0221	104.574 ± 14.601	1.6141 ± 0.2569
Total	CTRL	89.988 ± 3.871	0.7472 ± 0.0688	55.954 ± 2.707	0.4642 ± 0.0362	3.714 ± 0.671	0.031 ± 0.0071	1.844 ± 0.607	0.0155 ± 0.0059	2.419 ± 0.522	0.0202 ± 0.0051	1.312 ± 0.984	0.0108 ± 0.0077	83.247 ± 5.343	0.6905 ± 0.0591	2.423 ± 0.603	0.0203 ± 0.0062	240.901 ± 14.325	1.9996 ± 0.1883
	NaClO (0.5) 1h	90.349 ± 2.017	0.6907 ± 0.0366	55.367 ± 0.504	0.4231 ± 0.014	4.161 ± 0.152	0.0318 ± 0.0009	2.543 ± 0.048	0.0194 ± 0.0006	2.438 ± 0.924	0.0188 ± 0.0076	0.856 ± 0.636	0.0067 ± 0.005	80.259 ± 47.315	0.6216 ± 0.3754	4.267 ± 5.11	0.0318 ± 0.0373	240.24 ± 45.361	1.8439 ± 0.4027
	NaClO (0.5) 3h	100.354 ± 15.592	0.7823 ± 0.1557	60.926 ± 9.304	0.475 ± 0.0943	4.834 ± 0.77	0.0377 ± 0.0076	2.989 ± 0.689	0.0234 ± 0.0064	3.261 ± 1.195	0.0256 ± 0.0104	0.97 ± 1.236	0.0079 ± 0.0102	112.288 ± 20.771	0.877 ± 0.2086	5.55 ± 2.75	0.0425 ± 0.0203	291.171 ± 47.135	2.2712 ± 0.4765
	ClO_2 (0.5) 1h	90.467 ± 9.859	1.2091 ± 0.4701	56.139 ± 5.536	0.7492 ± 0.2826	3.67 ± 0.724	0.0497 ± 0.0234	2.09 ± 0.529	0.0286 ± 0.0149	0.708 ± 0.993	0.0114 ± 0.0169	0.317 ± 0.549	0.0053 ± 0.0092	31.742 ± 51.062	0.5209 ± 0.8583	7.755 ± 6.429	0.0894 ± 0.0791	192.889 ± 61.684	2.6637 ± 1.5587
	ClO_2 (0.5) 3h	87.045 ± 1.627	1.1403 ± 0.0839	54.32 ± 1.471	0.7116 ± 0.0541	3.779 ± 0.252	0.0493 ± 0.0008	2.367 ± 0.147	0.0311 ± 0.0037	0.161 ± 0.046	0.0021 ± 0.0007	<LOD	<LOD	4.352 ± 3.035	0.0567 ± 0.038	26.723 ± 7.932	0.3532 ± 0.1236	178.748 ± 10.074	2.3443 ± 0.2569
	ClO_2 (2.0) 1h	52.74 ± 4.226	0.8091 ± 0.0988	35.404 ± 2.892	0.5427 ± 0.0614	2.132 ± 0.406	0.0324 ± 0.0039	1.244 ± 0.433	0.0187 ± 0.0044	0.018 ± 0.007	0.0003 ± 0.0001	<LOD	<LOD	0.502 ± 0.216	0.0078 ± 0.0039	10.003 ± 0.847	0.1531 ± 0.0132	102.044 ± 8.666	1.564 ± 0.1781
	ClO_2 (2.0) 3h	55.406 ± 7.184	0.8555 ± 0.1332	36.483 ± 5.35	0.5627 ± 0.0889	2.147 ± 0.568	0.0331 ± 0.0086	1.172 ± 0.543	0.0181 ± 0.0081	0.005 ± 0.005	0.0001 ± 0.0001	<LOD	<LOD	0.334 ± 0.059	0.0051 ± 0.0004	9.731 ± 1.003	0.1504 ± 0.0222	105.277 ± 14.644	1.625 ± 0.2587

Table S5. Assignment of product ions detected in CID and HCD LC-HRMS^{2,3} spectra of cyanopeptolin-type peptide-1045 (CPtp-1045) (see Fig. S3-S5).

CPtp-1045	***m/z***	**Formula**	**Sequence**	**Neutral loss**
$[M+H]^+$	1046.5222	$C_{52}H_{72}O_{14}N_9^+$	[Choi^{1}+Gln^{2}+Ahp^{3}+Phe^{4}+NMeTyrOH^{5}+Leu/Ile^{6}+Hyp^{7}+Ala^{8}+H]$^+$	
$[M+H–H_2O]^+$	1028.5110	$C_{52}H_{70}O_{13}N_9^+$		H_2O
	1011.4814	$C_{52}H_{67}O_{13}N_8^+$		H_2O+NH_3
	1010.4989	$C_{52}H_{68}O_{12}N_9^+$		$2H_2O$
CID	897.4142	$C_{46}H_{57}O_{11}N_8^+$	[Hyp^{7}+Ala^{8}+Choi^{1}+Gln^{2}+Ahp^{3}+Phe^{4}+NMeTyr^{5}+H–2H$_2$O]$^+$	Leu/Ile^{6}+2H$_2$O
	786.4038	$C_{38}H_{56}O_{11}N_7^+$	[Gln^{2}+ Choi^{1}+Ala^{8}+Hyp^{7}+Leu/Ile^{6}+NMeTyr^{5}+H]$^+$	Ahp^{3}+Phe^{4}
	768.3923	$C_{38}H_{54}O_{10}N_7^+$	[Gln^{2}+ Choi^{1}+Ala^{8}+Hyp^{7}+Leu/Ile^{6}+NMeTyr^{5}+H–H$_2$O]$^+$	Ahp^{3}+Phe^{4}+H$_2$O
	733.3561	$C_{38}H_{49}O_9N_6^+$	[Choi^{1}+Gln^{2}+Ahp^{3}+Phe^{4}+NMeTyrOH^{5}+H–H$_2$O]$^+$	Leu/Ile^{6}+Hyp^{7}+Ala^{8}+H$_2$O
	715.3443	$C_{38}H_{47}O_8N_6^+$	[Choi^{1}+Gln^{2}+Ahp^{3}+Phe^{4}+NMeTyrOH^{5}+H–2H$_2$O]$^+$	Leu/Ile^{6}+Hyp^{7}+Ala^{8}+2H$_2$O
	593.3295	$C_{28}H_{45}O_8N_6^+$	[Gln^{2}+ Choi^{1}+Ala^{8}+Hyp^{7}+Leu/Ile^{6}+H–H$_2$O]$^+$	Ahp^{3}+Phe^{4}+NMeTyrOH^{5}+H$_2$O
	519.2243	$C_{28}H_{31}O_6N_4^+$	[Gln^{2}+Ahp^{3}+Phe^{4}+NMeTyrOH^{5}+H-CO-NH$_2$-H$_2$O]$^+$	Leu/Ile^{6}+Hyp^{7}+Ala^{8}+Choi^{1}+CO+NH$_2$+H$_2$O
	462.2349	$C_{22}H_{32}O_6N_5^+$	[Gln^{2}+ Choi^{1}+Ala^{8}+Hyp^{7}+H]$^+$	Ahp^{3}+Phe^{4}+NMeTyrOH^{5}+Leu/Ile^{6}
	436.1872	$C_{24}H_{26}O_5N_3^+$	[Ahp^{3}+Phe^{4}+NMeTyrOH^{5}+H–H$_2$O]$^+$	Choi^{1}+Gln^{2}+Leu/Ile^{6}+Hyp^{7}+Ala^{8}+H$_2$O
	296.1616^{a}	$C_{14}H_{22}O_4N_3^+$	[Choi^{1}+Gln^{2}+H]$^+$	Ahp^{3}+Phe^{4}+NMeTyrOH^{5}+Leu/Ile^{6}+Hyp^{7}+Ala^{8}
HCD	243.1130	$C_{14}H_{15}O_2N_2^+$	[Ahp^{3}+Phe^{4}+H–H$_2$O]$^+$	Choi^{1}+Gln^{2}+NMeTyrOH^{5}+Leu/Ile^{6}+Hyp^{7}+Ala^{8}+H$_2$O
	215.1182	$C_{13}H_{15}ON_2^+$	[Ahp^{3}+Phe^{4}+H–CO–H$_2$O]$^+$	Choi^{1}+Gln^{2}+NMeTyrOH^{5}+Leu/Ile^{6}+Hyp^{7}+Ala^{8}+CO+H$_2$O
	187.1232	$C_{12}H_{15}N_2^+$	[Ahp^{3}+Phe^{4}+H–2CO–H$_2$O]$^+$	Choi^{1}+Gln^{2}+NMeTyrOH^{5}+Leu/Ile^{6}+Hyp^{7}+Ala^{8}+2CO+H$_2$O
	168.1021^{a}	$C_9H_{14}O_2N^+$	[Choi^{1} (immonium ion)+CO+H]$^+$	Gln^{2}+Ahp^{3}+Phe^{4}+NMeTyrOH^{5}+Leu/Ile^{6}+Hyp^{7}+Ala^{8}
	166.0866	$C_9H_{12}O_2N^+$	[NMeTyrOH^{5}+H]$^+$	Choi^{1}+Gln^{2}+Ahp^{3}+Leu/Ile^{6}+Hyp^{7}+Ala^{8}
	140.1071^{a}	$C_8H_{14}ON^+$	[Choi^{1} (immonium ion)+H]$^+$	Gln^{2}+Ahp^{3}+Phe^{4}+NMeTyrOH^{5}+Leu/Ile^{6}+Hyp^{7}+Ala^{8}
	120.0808	$C_8H_{10}N^+$	[Phe^{4} (immonium ion)+H]$^+$	Choi^{1}+Gln^{2}+Ahp^{3}+NMeTyrOH^{5}+Leu/Ile^{6}+Hyp^{7}+Ala^{8}
	70.0650	$C_4H_8N^+$	[Hyp^{7} (immonium ion)+H]$^+$	Choi^{1}+Gln^{2}+Ahp^{3}+Phe^{4}+NMeTyrOH^{5}+Leu/Ile^{6}+Ala^{8}

^{a}Fragment confirmed also in LC-HRMS^{3} experiments, precursor ion at *m/z* 462.2343

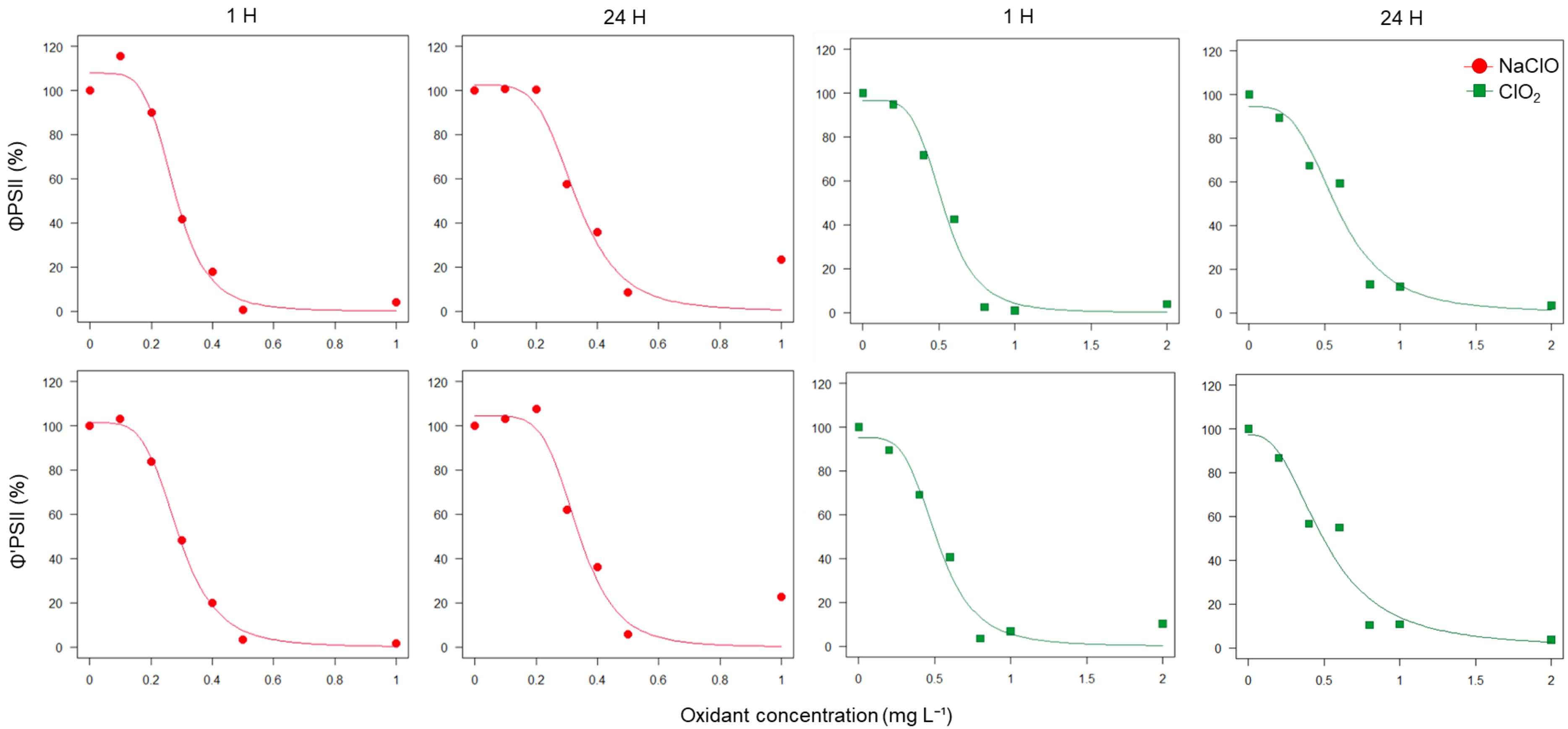


Fig. S1. EC_{50} dose-response curves for NaClO (red circles) ClO_2 (green squares) obtained from photosynthetic efficiency measurements after 1 and 24 h of treatment. The percent inhibition of the photosynthetic parameters was calculated from maximum quantum yield (ΦPSII) and effective quantum yield (Φ'PSII)

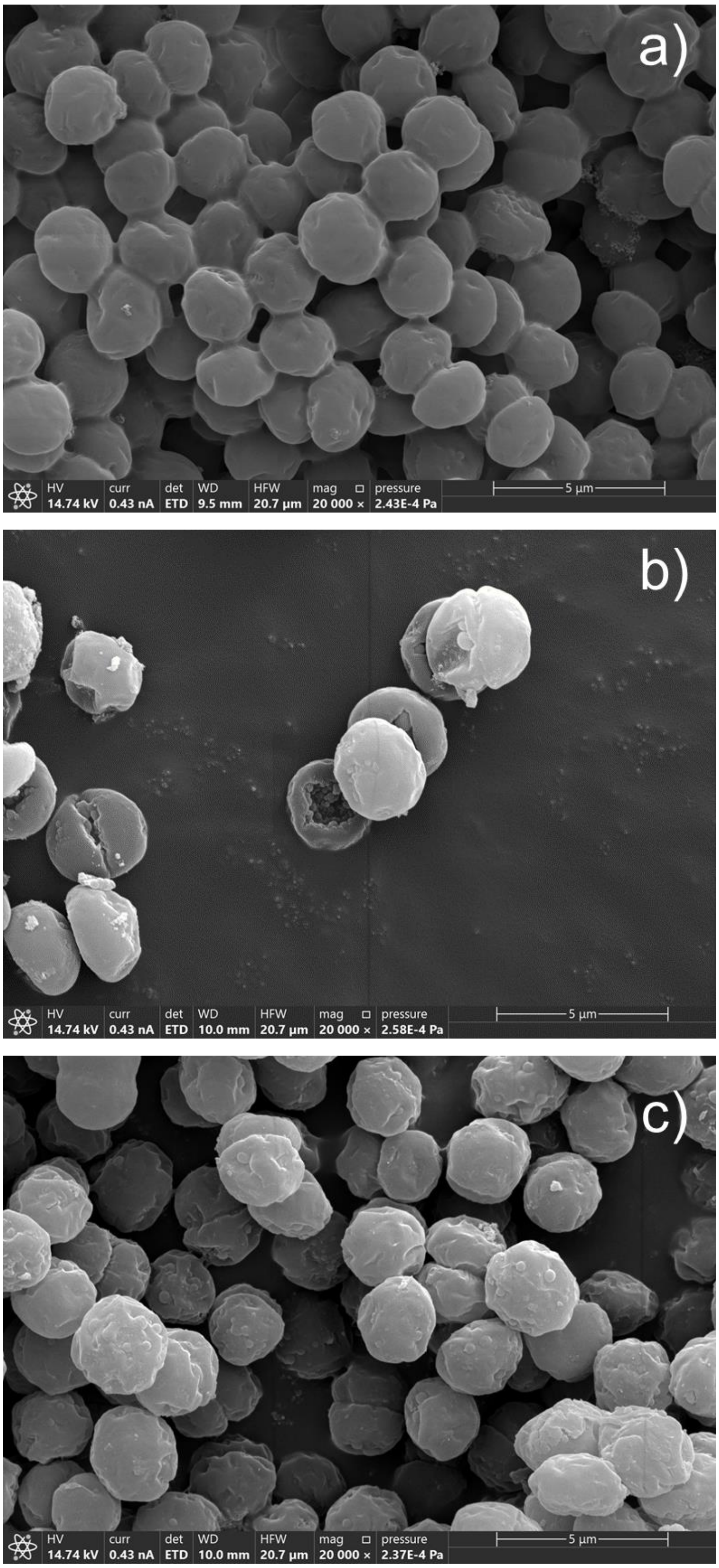
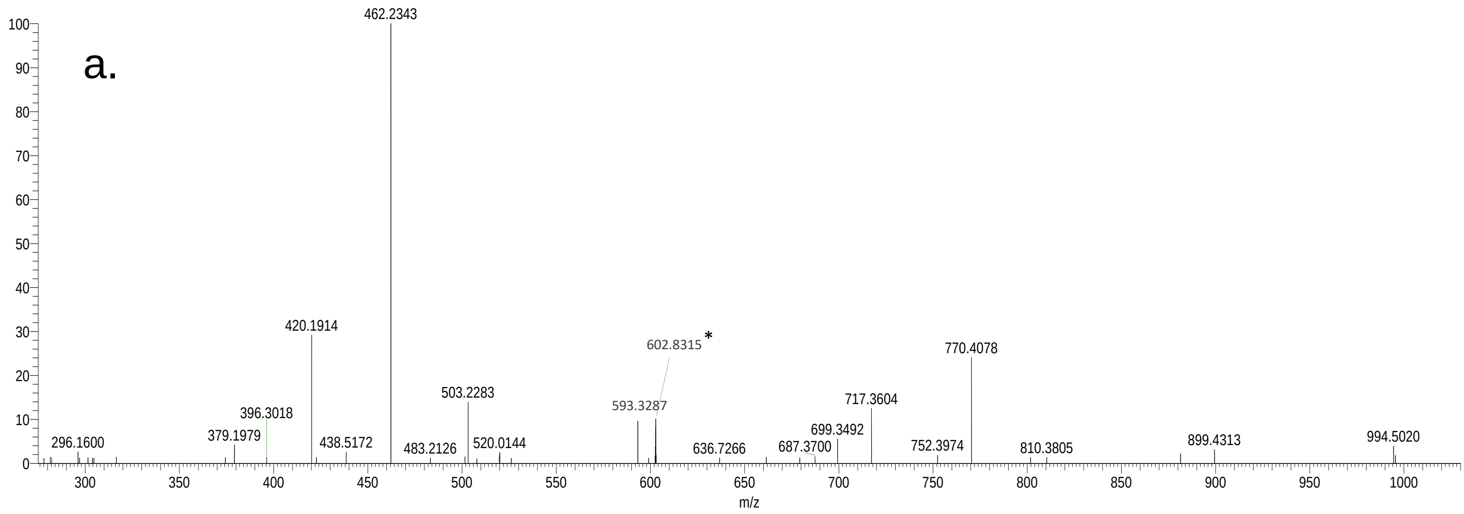


Fig. S2. Microscopic photographs of *M. aeruginosa* cells acquired through environmental scanning electron microscopy (ESEM) imaging, using a Field Emission Quattro S ESEM (Thermo Fisher, Waltham, USA). From top to bottom: a) controls, b) NaClO, and c) ClO_2 treated samples.



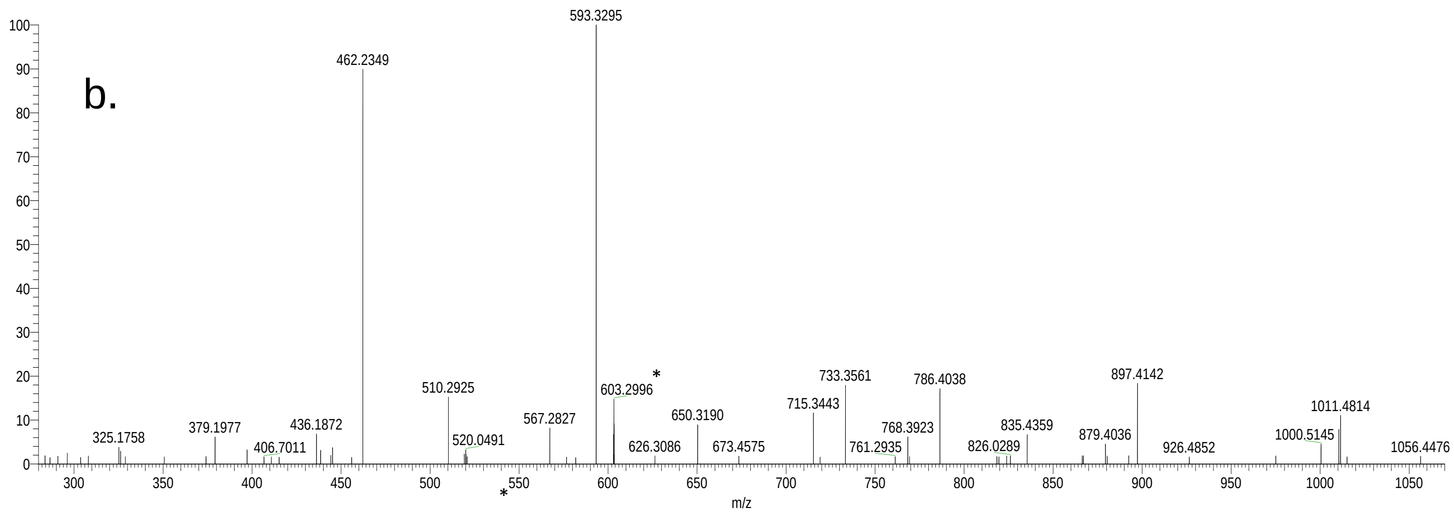


Fig. S3. CID HRMS[2] spectra acquired by selecting as precursor the $[M+H–H_2O]^+$ ion of a) CPtp-1029 at *m/z* 1012.5134 and b) CPtp-1045 at *m/z* 1028.5110. Collision energy, CE = 40%. * = Noise

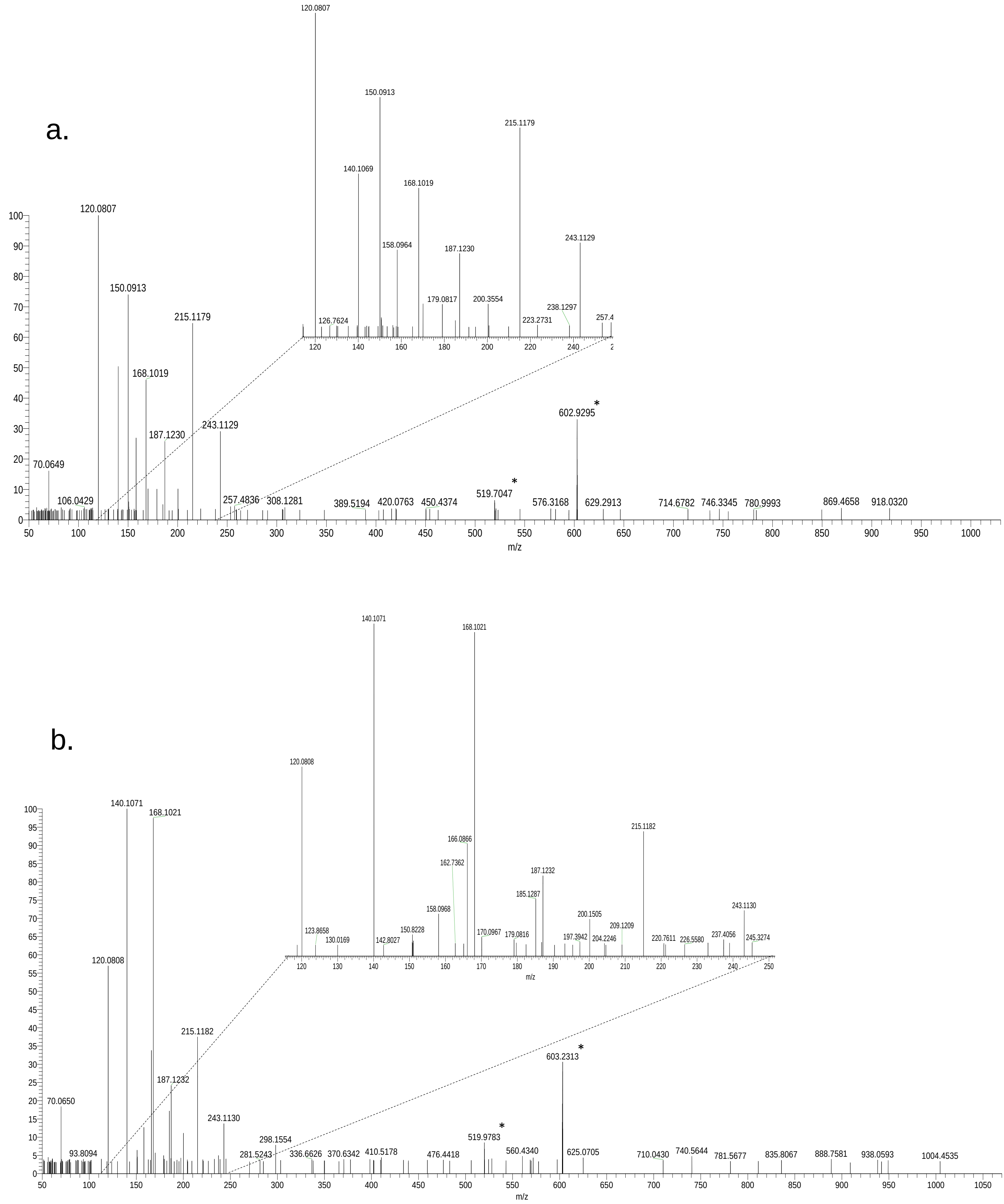


Fig. S4. HCD HRMS[2] spectra acquired by selecting as precursor the $[M+H–H_2O]^+$ ion of a) CPtp-1029 at *m/z* 1012.5134 and b) CPtp-1045 at *m/z* 1028.5110. Collision energy, CE = 40%. * = Noise

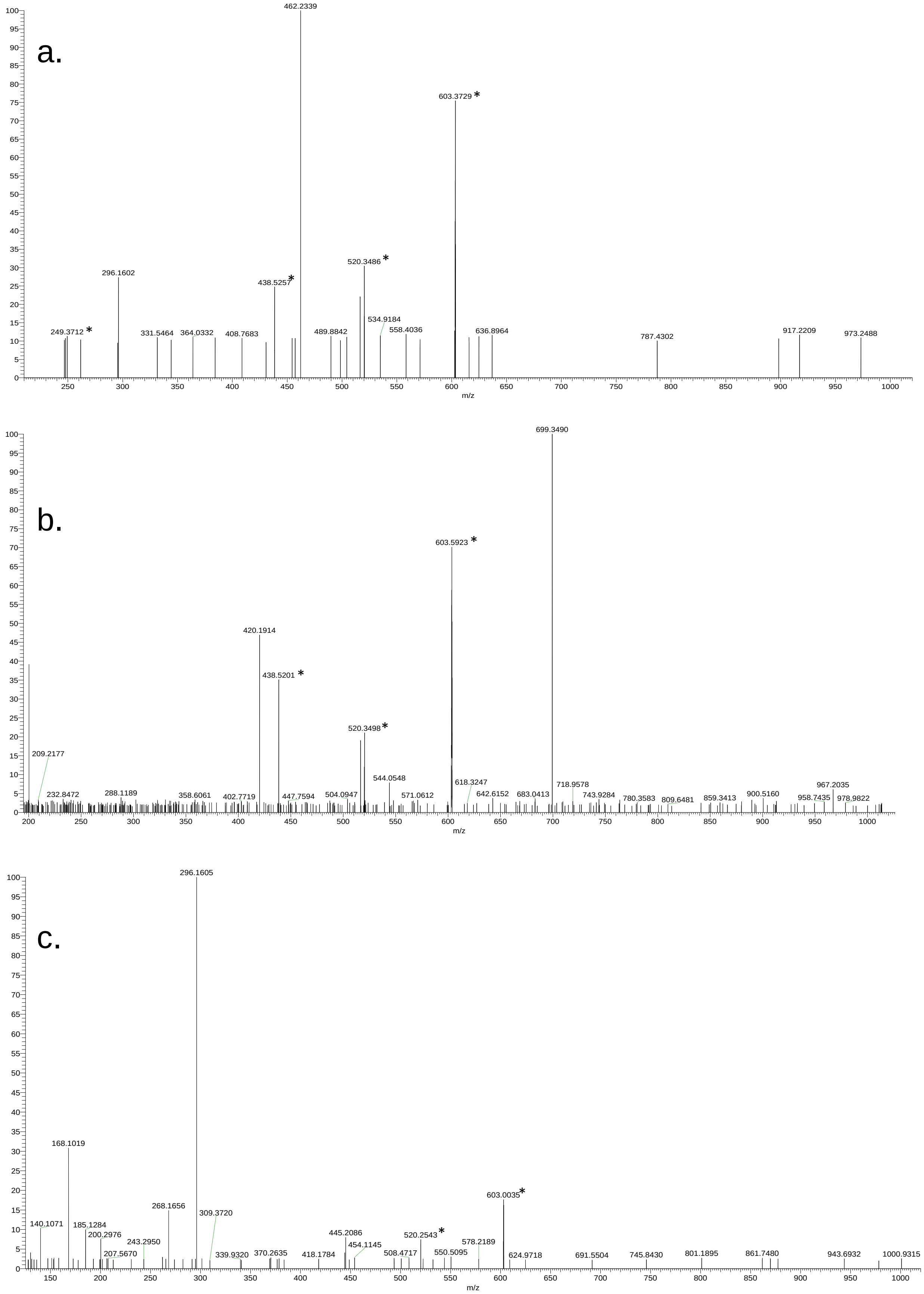


Fig. S5. CID HRMS^3 spectra of CPtp-1029 a) precursor ion at *m*/*z* 1012.5134 > 770.4078 (collision energy, CE = 78%) b) precursor ion at *m*/*z* 1012.5134 > 717.3604 (CE = 40%) and c) precursor ion at *m*/*z* 1012.5134 > 462.2343 (CE = 25%). * = Noise

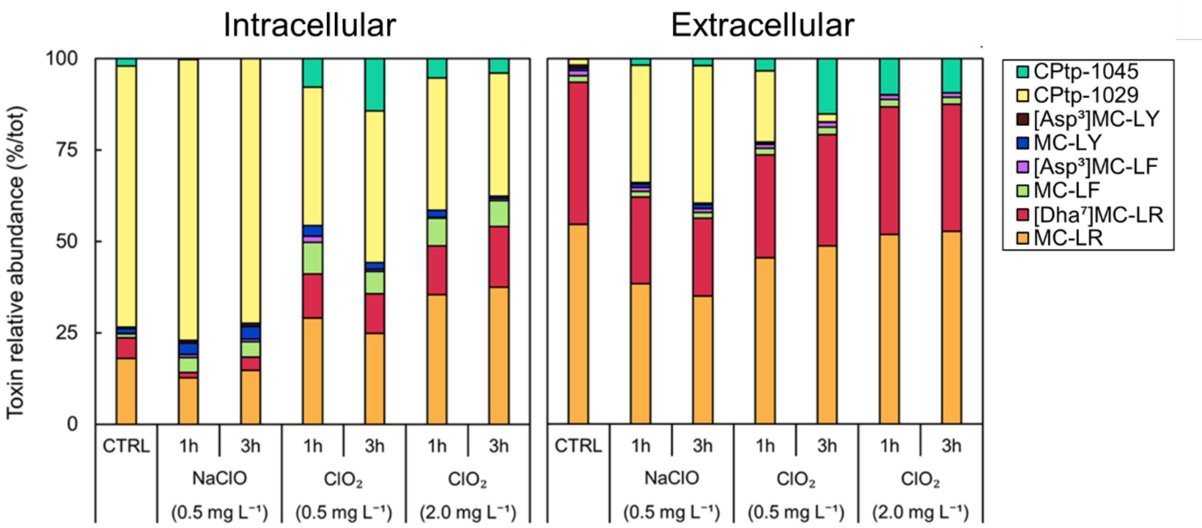


Fig. S6. Relative abundances of MCs variants and metabolites in *M. aeruginosa* cultures treated with NaClO and ClO_2 expressed as percentage on the total toxin content (pg cell^{-1}) in both intracellular and extracellular fractions. CPtp-1029 = cyanopeptolin-type peptide-1029, CPtp-1045 = cyanopeptolin-type peptide-1045