Supporting Information

Analysis of multiclass cyanotoxins (microcystins, anabaenopeptins, cylindrospermopsin and anatoxins) in lake waters using on-line SPE liquid chromatography high-resolution Orbitrap mass spectrometry

Audrey Roy-Lachapelle[1,2], Sung Vo Duy[1], Gabriel Munoz[1], Quoc Tuc Dinh[1], Emmanuelle Bahl[1], Dana F. Simon[1], Sébastien Sauvé[1]*

[1] Department of Chemistry, Université de Montréal, Montreal, Québec H3C 3J7, Canada.

[2] Aquatic Contaminants Research Division, Environment and Climate Change Canada, 105 McGill, Montréal, Québec H2Y 2E7, Canada.

[*]Corresponding author. Phone: 514-343-6710; E-mail: sebastien.sauve@umontreal.ca. Department of Chemistry, Université de Montréal, Montreal, Québec H3C 3J7, Canada

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Table S1. Summary of the method accuracy (%) and precision (relative standard deviation, RSD %) investigated at 4 spike levels in lake surface water (75, 120, 200 and 800 ng L^{-1}).

Cyanotoxins	**Accuracy (%)**				**Intra-day precision (RSD, %)**				**Inter-day precision (RSD, %)**			
	Spike level (ng L^{-1})				*Spike level (ng L^{-1})*				*Spike level (ng L^{-1})*			
	75	*120*	*200*	*800*	*75*	*120*	*200*	*800*	*75*	*120*	*200*	*800*
CYN	<LOQ	<LOQ	86 ± 9	103 ± 5	<LOQ	<LOQ	10	4.5	<LOQ	<LOQ	10.5	7.2
ANA-a	98 ± 4	101 ± 7	96 ± 7	103 ± 2	4.6	7.2	7.6	2.3	5.5	6.5	7.9	4.7
HANA-a	90 ± 4	94 ± 4	85 ± 4	97 ± 2	4	4.8	4.5	2.3	7.1	6.6	4.5	5.3
AP-A	96 ± 9	105 ± 11	107 ± 7	99 ± 3	9.4	10.9	6.6	3.3	13.5	8	5.4	5.2
AP-B	103 ±7	101 ± 7	92 ± 4	98 ± 8	7	6.8	4.8	7.9	8.2	6.4	4.4	6.9
[Asp³]MC-RR	94 ± 7	86 ± 5	81 ± 5	86 ± 4	7.9	5.9	6.4	4.8	12.1	7.5	5.1	6.8
MC-RR	86 ± 3	82 ± 3	81 ± 4	91 ± 1	3	4.1	4.6	1.2	8.8	6.6	4.6	4
MC-YR	<LOQ	106 ± 7	104 ± 6	102 ± 5	<LOQ	6.4	6.2	4.9	<LOQ	5.9	6.8	4.9
MC-HtyR	<LOQ	112 ± 7	113 ± 5	107 ± 3	<LOQ	6.1	4.7	2.6	<LOQ	5.9	4.8	4.4
MC-LR	100 ± 14	102 ± 9	99 ± 4	107 ± 6	13.7	8.9	3.8	5.2	10.2	6.8	4.2	4.7
[Asp³]MC-LR	101 ± 7	100 ± 5	94 ± 2	97 ± 5	6.8	5.5	2.5	5.4	6.6	5.1	3.1	4.9
MC-HilR	94 ± 11	99 ± 6	100 ± 5	101 ± 6	12.2	6.1	4.6	6	9	6.1	6.2	5
MC-WR	<LOQ	93 ± 16	102 ± 5	93 ± 6	<LOQ	16.9	5.1	6.1	<LOQ	12.8	6.7	5.9
MC-LA	97 ±10	94 ± 8	89 ± 7	100 ± 2	9.9	8.6	7.3	2.5	10.6	7.9	7.5	4.7
MC-LY	<LOQ	85 ± 41	121 ± 20	106 ± 5	<LOQ	48.4	16.1	4.3	<LOQ	31.3	11.7	5.6
MC-LW	<LOQ	100 ± 7	102 ± 11	94 ± 5	<LOQ	7.4	11.1	5.8	<LOQ	10.5	9.4	6
MC-LF	<LOQ	107 ± 17	106 ± 14	106 ± 8	<LOQ	16.3	13.1	7.2	<LOQ	18.6	11.9	5.4

Table S2. Details on semi-quantified concentrations (ng L^{-1}) of qualitatively detected MCs from the present survey (ND: analyte not detected).

	[M(O)^1,Glu(OCH$_3$)^6]MC-LR	**[ADMAdda^5, Dha^7]MC-LR**	**MC-HphHty**
Lac Juneau	ND	ND	ND
Lac aux Bouleaux	**41**	ND	ND
Lac Moffatt	ND	ND	ND
Roxton Pond	**34**	ND	ND
Reservoir Choinière	ND	ND	ND
Lac Brome	ND	ND	ND
Lac Memphremagog	**7500**	**1700**	**1500**
Lac Waterloo	ND	ND	ND
Lac à la Tortue	ND	ND	ND
Lac McKay	ND	ND	ND
Lac Phonegamook	ND	ND	ND
Lac aux Cygnes	ND	ND	ND
Lac René	ND	ND	ND
Lac des Iles	ND	ND	ND
Muskrat Lake, ON	ND	**17**	**15**
Lac Mimi	ND	ND	ND

Figure S1. Improvement in analyte identification using high-resolution MS/MS for difficult-to-measure compounds, illustrated for MC-LW and MC-LA. The high-resolution MS/MS fragment ions followed for MC-LW and MC-LA in PRM (Table S2) correspond to $[M+H-134]^+$ (loss of the Adda fragment). MC-LW (left panels) was analyzed in non-spiked surface water using Full Scan (**a**) *vs.* PRM (**b**), and in surface water spiked at 50 ng L^{-1} using Full Scan (**c**) *vs.* PRM (**d**). MC-LA (right panels) was analyzed in non-spiked surface water using Full Scan (**e**) *vs.* PRM (**f**), and in surface water spiked at 50 ng L^{-1} using Full Scan (**g**) *vs.* PRM (**h**).

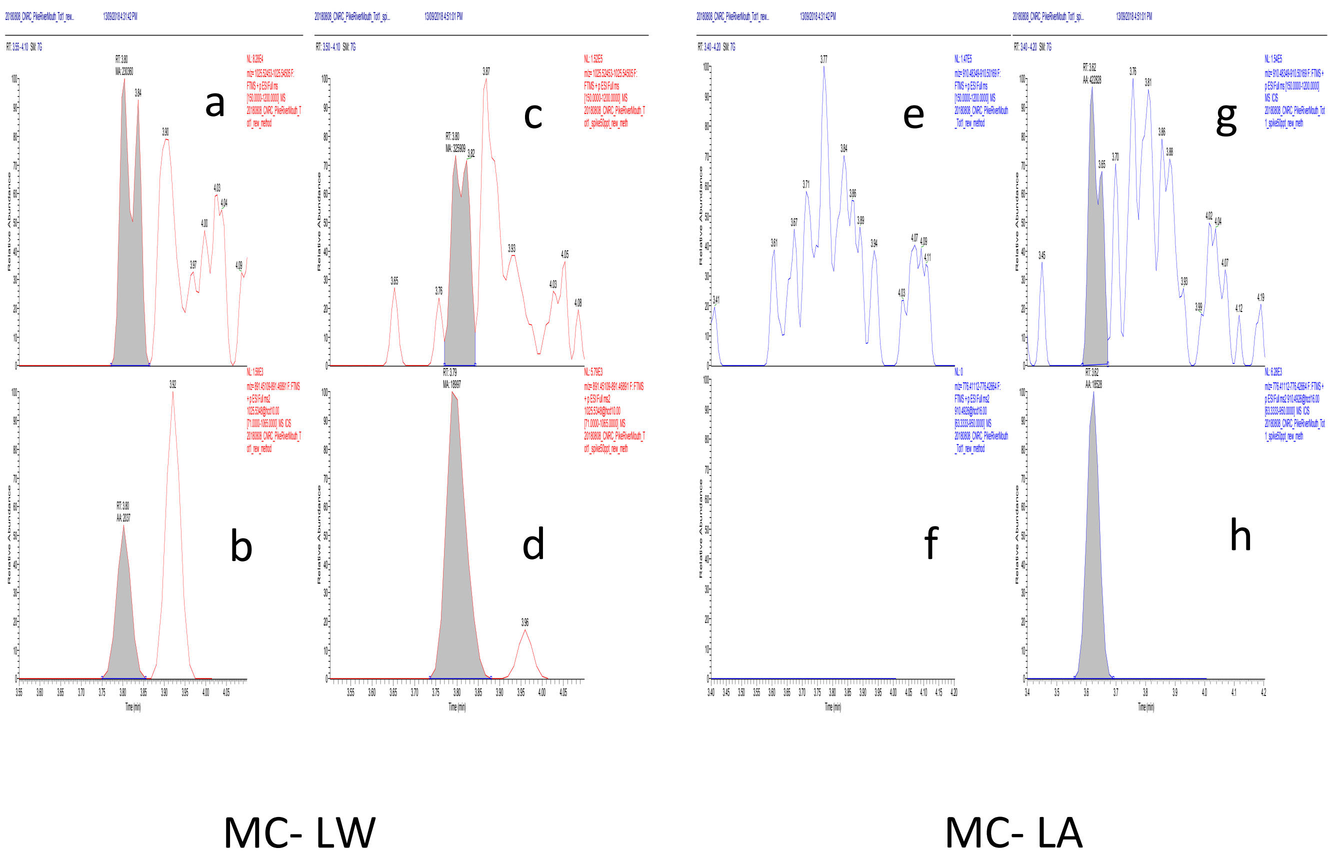

Figure S2. Extracted UHPLC-HRMS chromatograms in full scan MS mode and corresponding mass spectrum for qualitatively detected peak m/z 1085.5700 (observed m/z: 1085.5675) in surface water from Lake Memphrémagog. A mass tolerance of ± 5 ppm was applied. Tentative candidate: [M(O)^1, Glu(OMe)^6]MC-LR.