

## Supporting Information

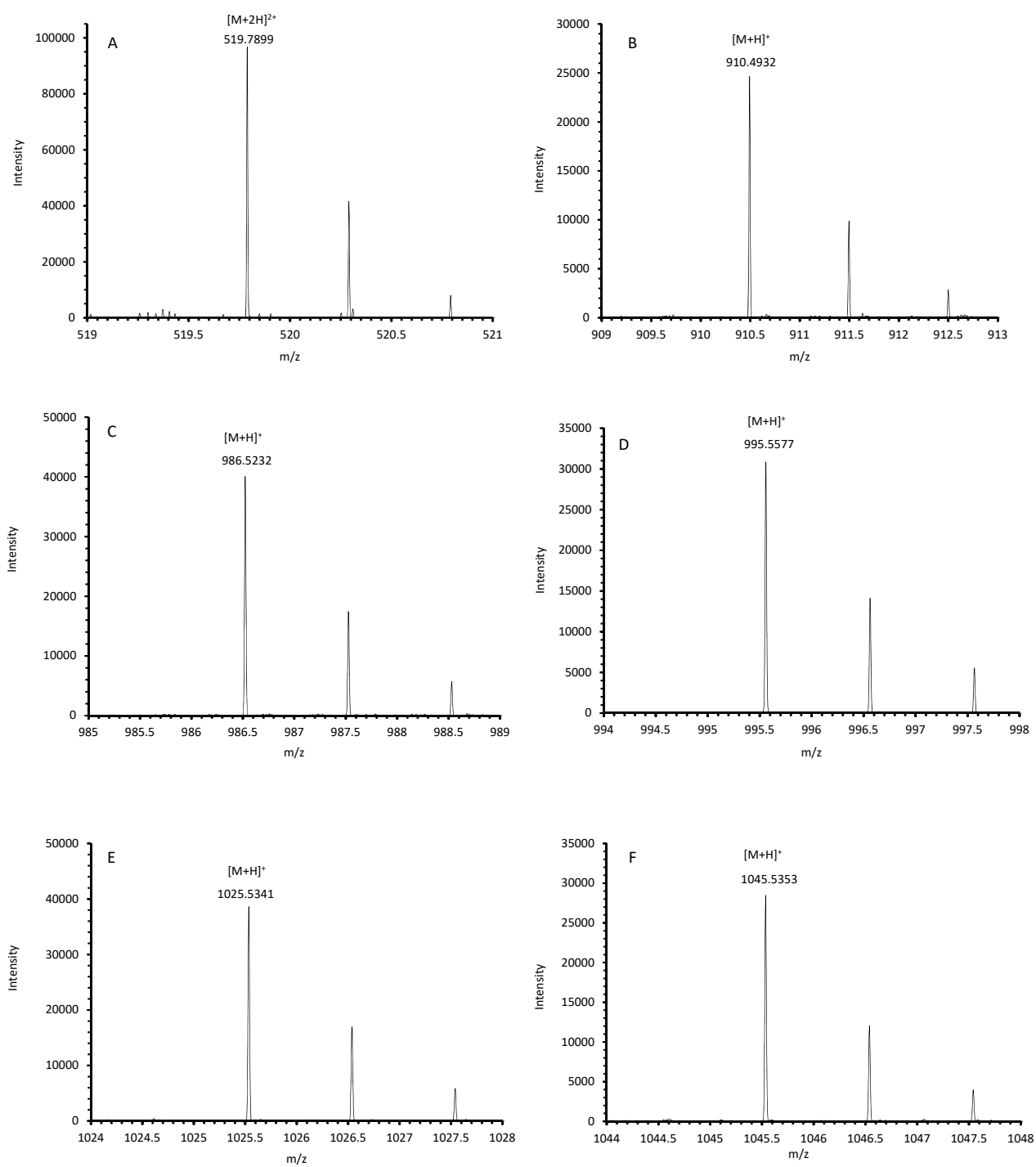
### Improved solid-phase extraction protocol and sensitive quantification of six microcystins in water using an HPLC-orbitrap mass spectrometry system

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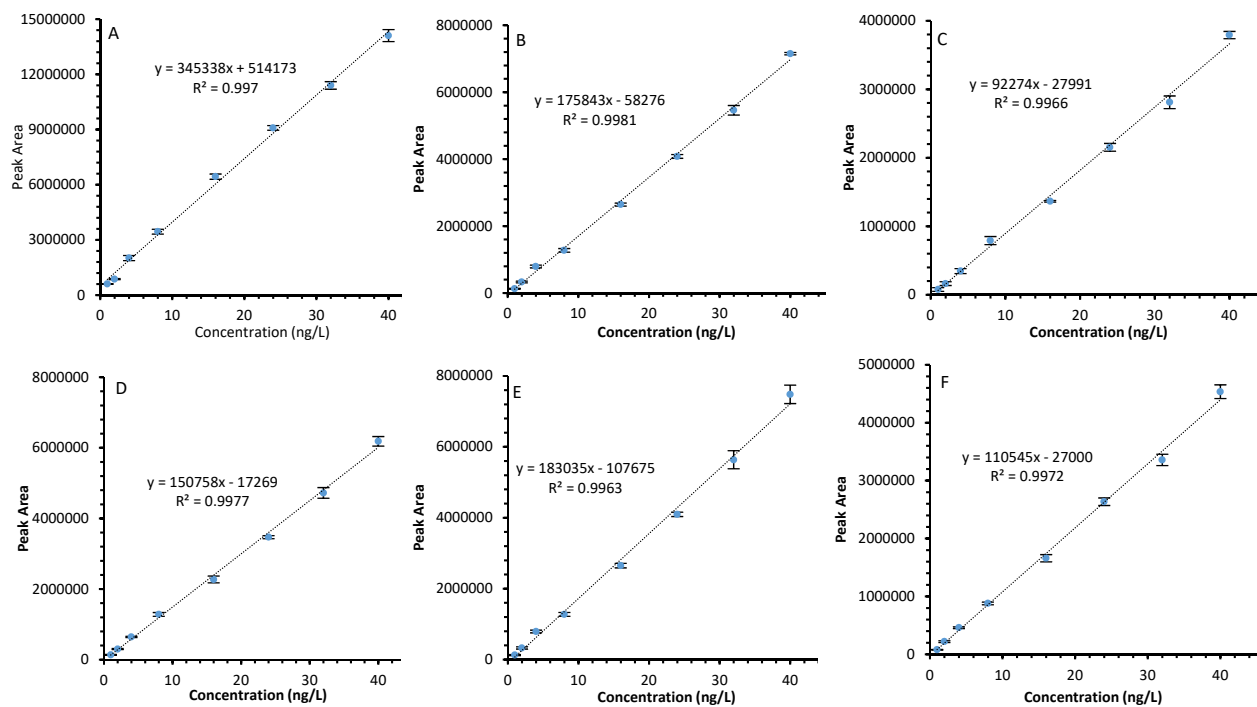
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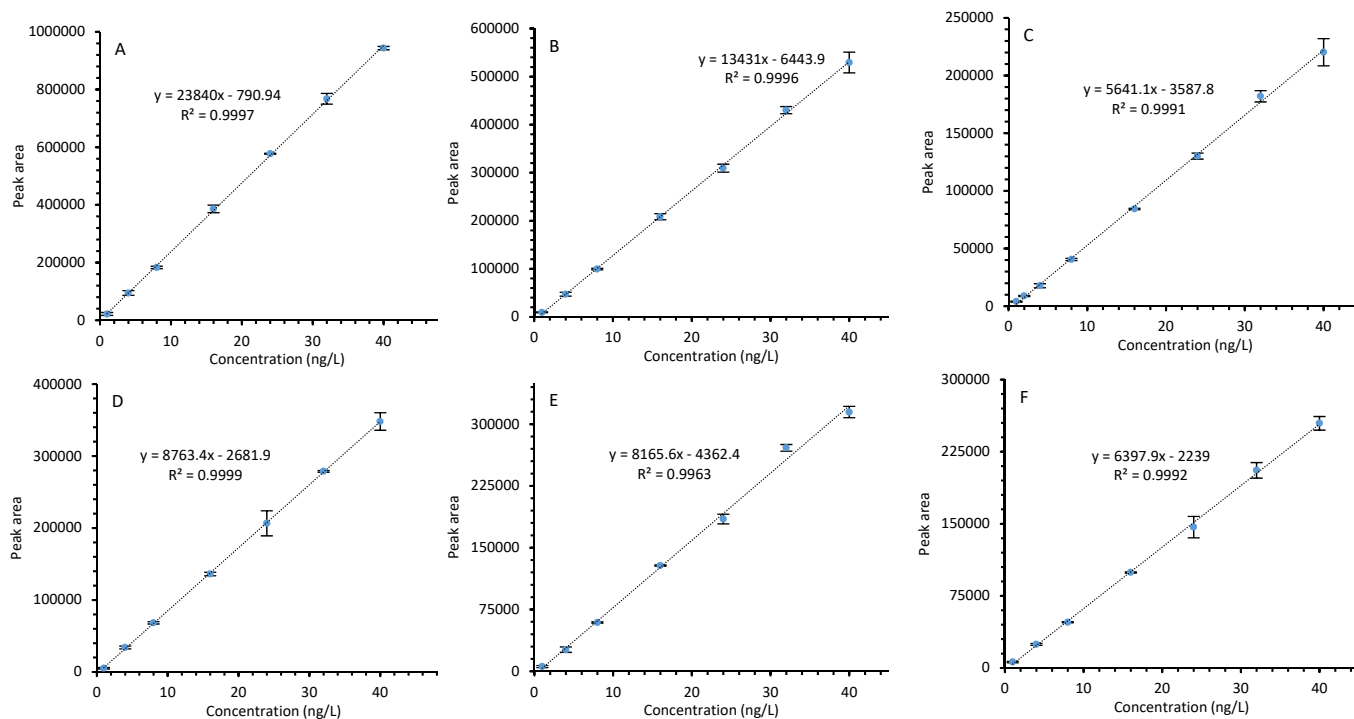
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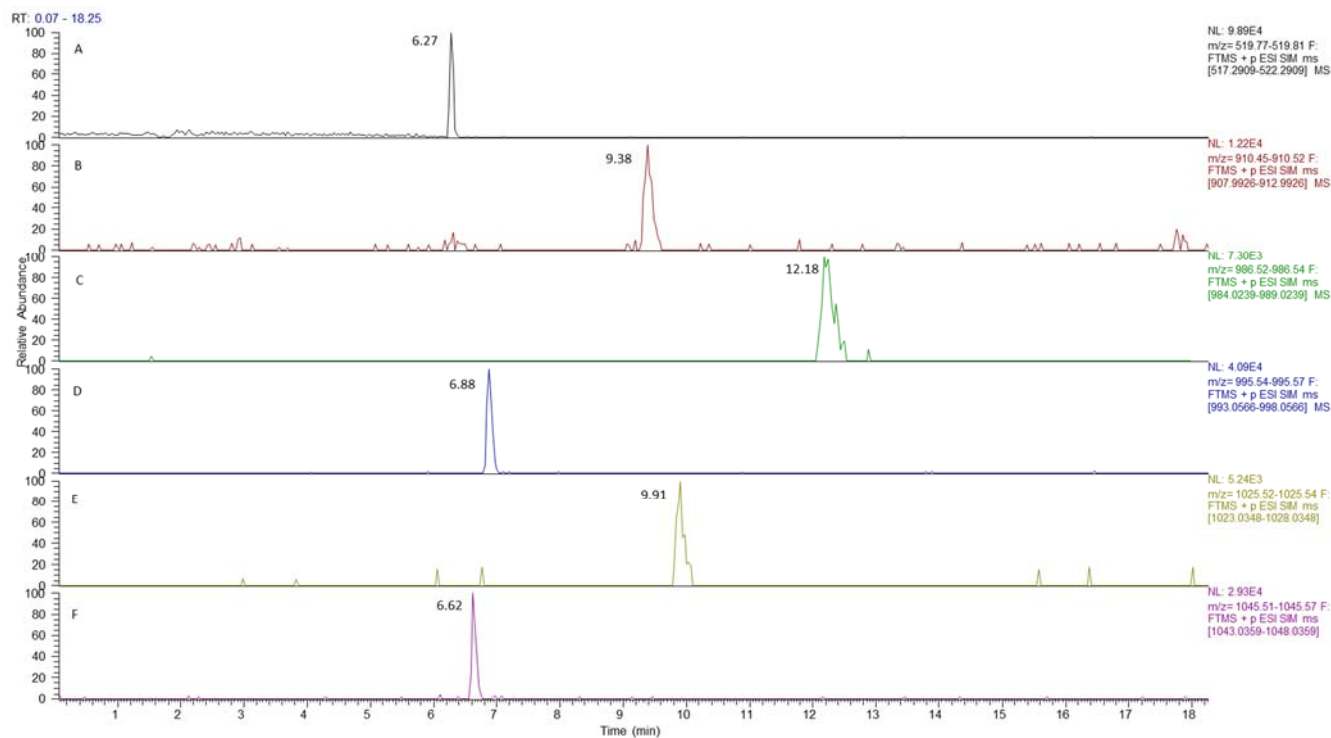
**Fig. S1.** SIM mass spectra of (A) MC-RR, (B) MC-LA, (C) MC-LF, (D) MC-LR, (E) MC-LW, and (F) MC-YR



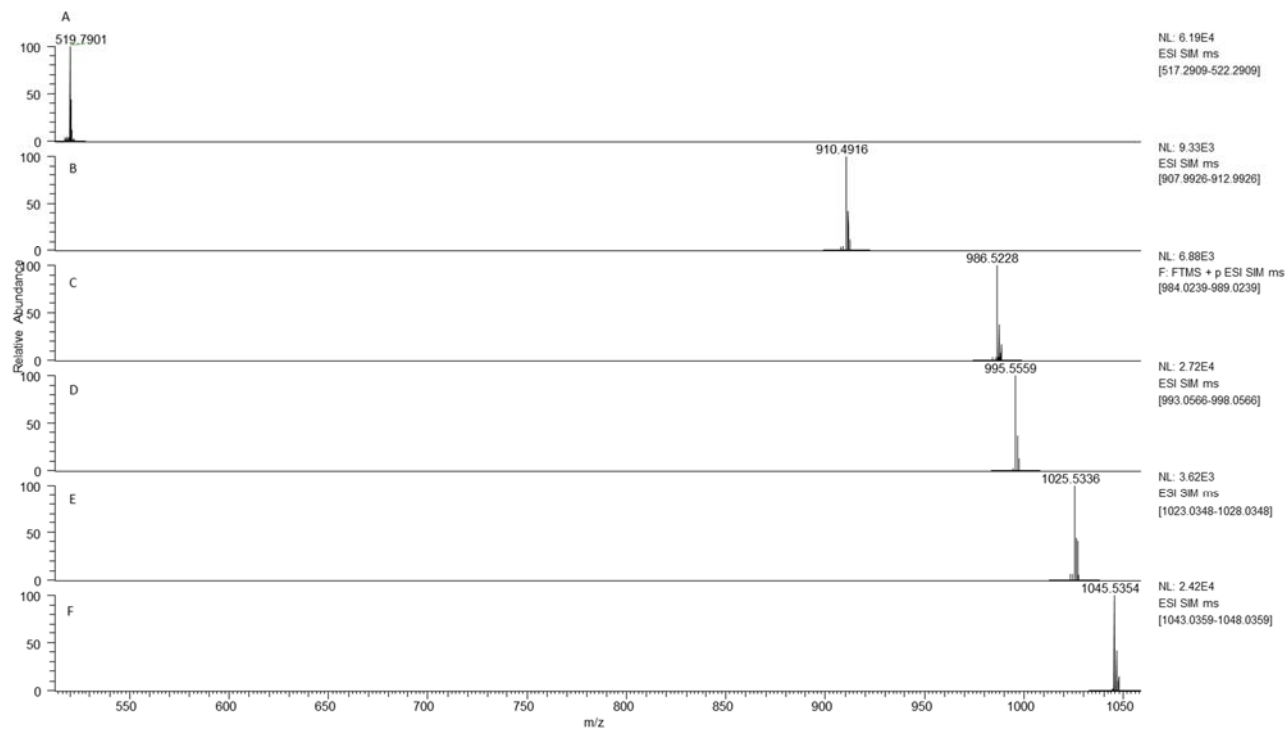
**Fig. S2.** The LC-ESI-MS calibration curves for quantification of (A) MC-RR, (B) MC-LA, (C) MC-LF, (D) MC-LR, (E) MC-LW, and (F) MC-YR in a mixture of MCs in tap water after 25x preconcentration. Error bars represent standard deviations of EIC peak areas of MC monoisotopic ions ( $n=3$ ).



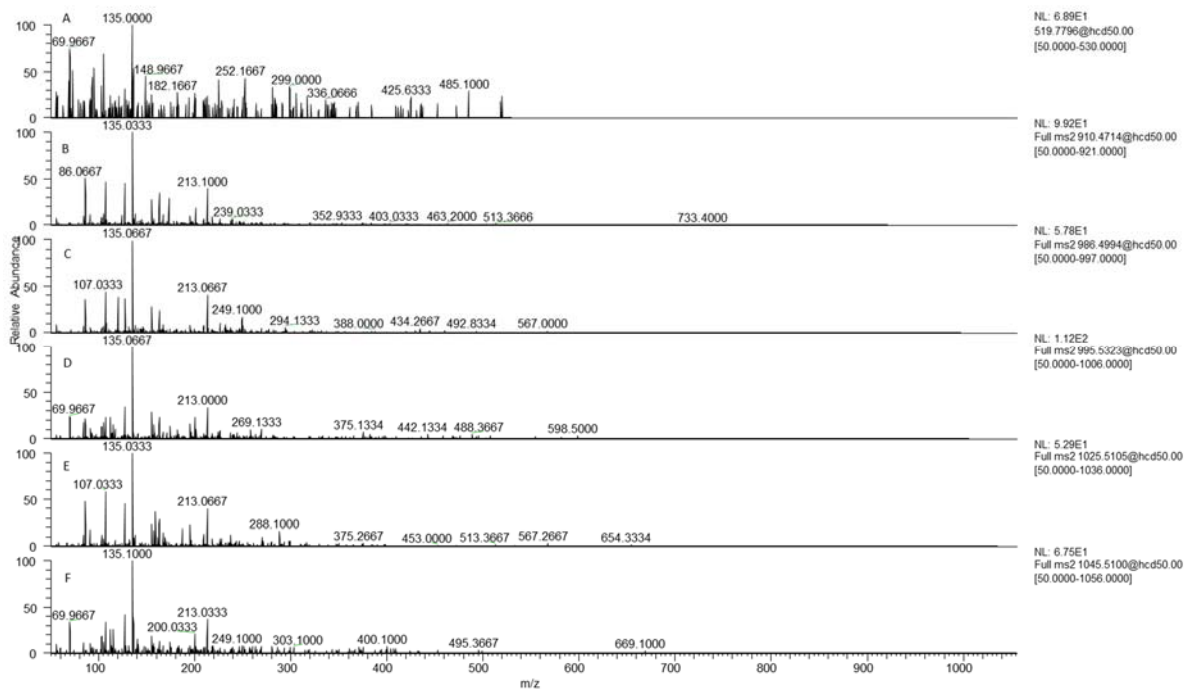
**Fig. S3.** The LC-ESI-MS calibration curves for quantification of (A) MC-RR, (B) MC-LA, (C) MC-LF, (D) MC-LR, (E) MC-LW, and (F) MC-YR in a mixture of MCs in lake water after 25x preconcentration. Error bars represent standard deviations of EIC peak areas of MC monoisotopic ions (n=3).



**Fig. S4.** The EICs corresponding to separation of (A) MC-RR, (B) MC-LA, (C) MC-LF, (D) MC-LR, (E) MC-LW, and (F) MC-YR from the solution containing 1 ng/L of each MC in lake water. After 25x preconcentration, the concentration of each MC in this solution was ~25 ng/L.



**Fig. S5.** SIM mass spectra of (A) doubly-charged MC-RR ion and singly-charged (B) MC-LA, (C) MC-LF, (D) MC-LR, (E) MC-LW, and (F) MC-YR ions, whose  $m/z$  values are 519.7901, 910.4916, 986.5228, 995.5559, 1025.5336, and 1045.5354, respectively. Spectra were obtained from EICs of six MCs shown in Fig. S4.



**Fig. S6.** SIM-MS/MS spectra of (A) doubly-charged MC-RR ion and singly-charged (B) MC-LA, (C) MC-LF, (D) MC-LR, (E) MC-LW, and (F) MC-YR ions, whose  $m/z$  values are 519.7901, 910.4916, 986.5228, 995.5559, 1025.5336, and 1045.5354, respectively.