Supplementary Information

A highly sensitive ultra-performance liquid chromatography coupled with triple quadrupole mass spectrometry detection method for levoglucosan based on Na^+ enhancing its Ionization efficiency

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Optimization of experimental condition

Column selection

Eclipse Plus C18 RRHD (2.1 x× 50 mm, 1.8 um, Agilent, USA) column was first selected for detection, but levoglucosan was barely retained on the C18 column, thus unable to separate the target substance and eliminate the interference of impurities in the matrix. Hence, a BEH Amide column (2.1×*100 mm, 1.7 um, Waters, USA) was chosen in this method to carry out the following analysis due to its excellent separation ability of small molecules of carbohydrate.

Column temperature optimization

Comparative experiments showed that signal intensity increased with the rising of temperature when temperature ranged of 25 to 40 °C(Fig.S1). Considering the increasing column temperature may accelerate column bleeding, the column temperature was chosen as 40 °C in this study.

Optimization of the composition, elution gradient and flow rate of mobile phase

The results showed that 0.1% formic water had a gain effect on the response of levoglucosan, while there were little difference use methanol or acetonitrile as the organic phase. In order to minimize the solvent effect, 0.1% formic water -methanol were finally selected as the mobile phase.

The response of levoglucosan increased slightly when the concentration of formic acid increased from 0.1 to 0.5 (Fig.S2). Considering the optimal pH range for the column and the gain degree of large concentration of formic acid on the signal, we finally decided to choose 0.1% formic acid and methanol as the mobile phase.

Since the precursor ion was used as the quantitative ion, impurity peaks interfering with integral quantitative in the separation process was presumable. In order to separate the target peak and the impurity peak preferably, we adjusted a series of gradients for comparison. However, it was found that the peak shape of levoglucosan would be interfered when organic phase ratio changing rapidly in gradient separation, which greatly

affected the qualitative analysis. Moreover, the increasing flow rate will lead to the focus of peaks and affect the separation degree of chromatographic peaks.

Optimization of sample filtration

At the beginning, polyether sulfone (PES) filter and online filter were used for sample filtration respectively, in order to reduce the matrix effect and the damage to the column from insoluble particles. However, comparative experiment result shows that filtered by polyether sulfone (PES) filter may cause partial sample loss (Fig.S3), moreover, sample residue was found on the filter when using the online filter, which will have a great influence on the detection of the next sample.

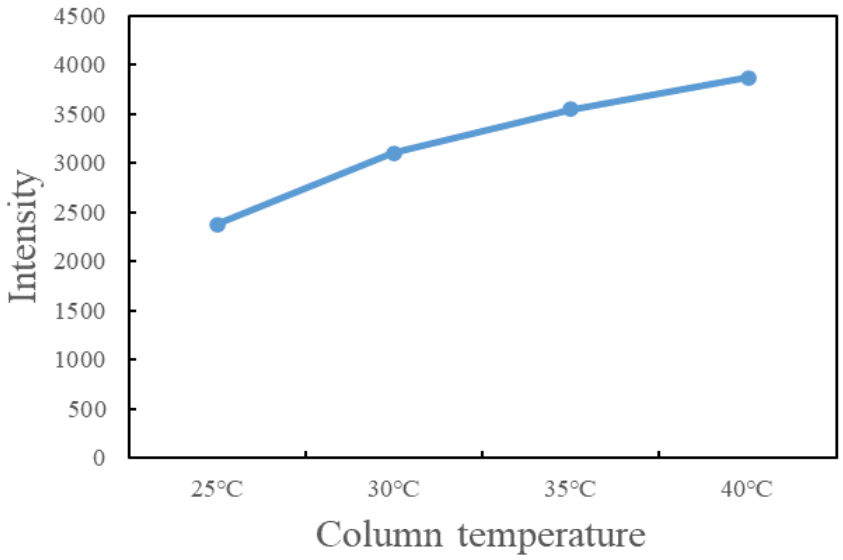

Fig.S1. Comparison of the response of levoglucosan standard solution in different column temperature

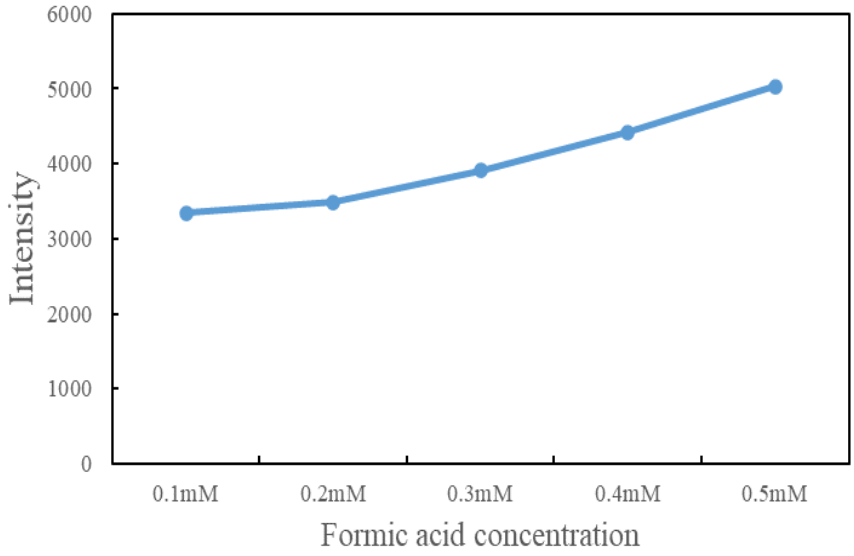

Fig.S2. Comparison of the response of levoglucosan standard solution in different formic acid concentration

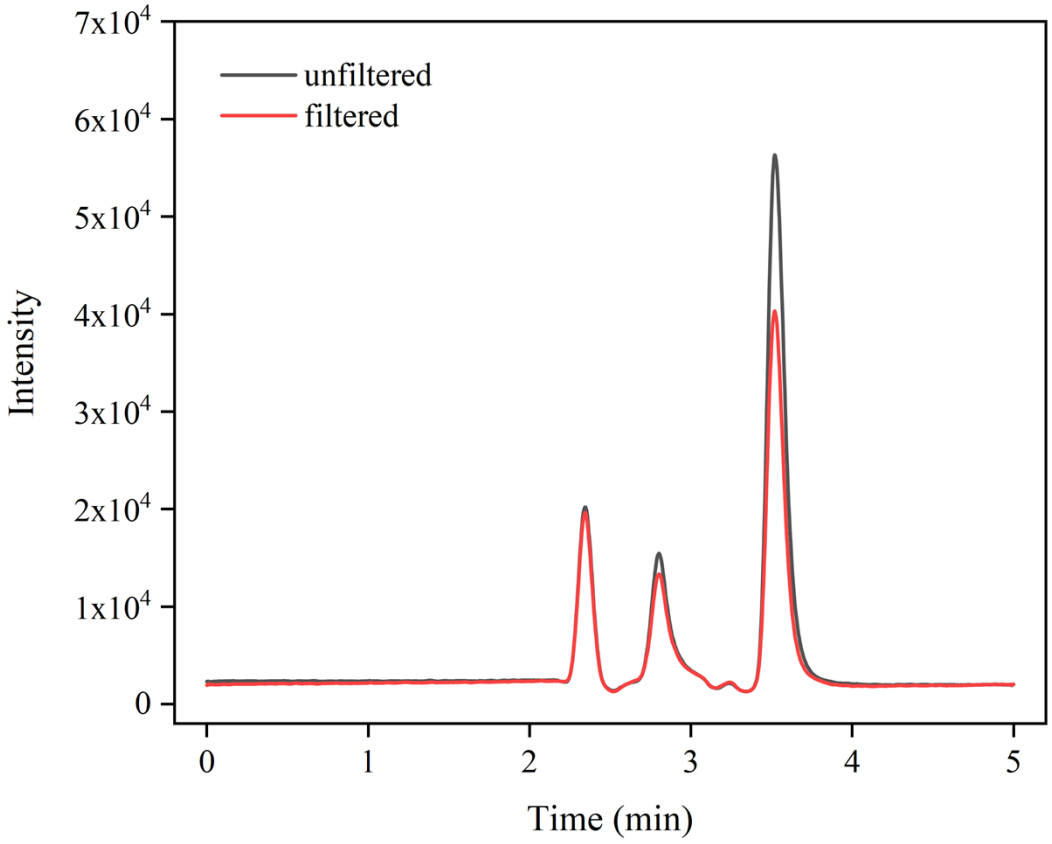

Fig.S3. Comparison of chromatogram of river water samples before and after filtration

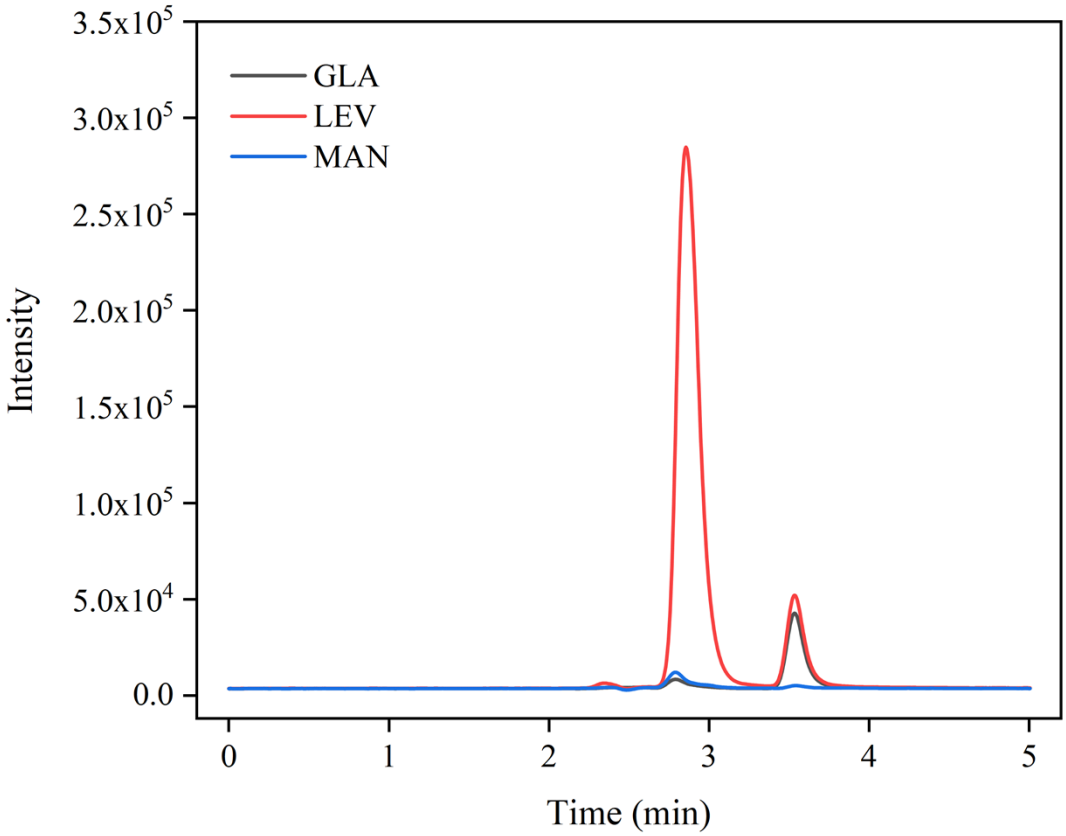

Fig.S4. Comparison of chromatogram of 1µg/mL standard solution of levoglucosan (LEV), mannosan (MAN) and galactosan (GAL)

TableS1 The repeatability detection results of levoglucosan standard solution

Standard solution	Retention time (min)	Concentration (ng /mL)	RSD
5ppb	2.893	4.704	5%
5ppb	2.893	4.7008	
5ppb	2.888	4.7222	
5ppb	2.897	4.7434	
5ppb	2.884	4.7058	
5ppb	2.893	4.7384	
5ppb	2.897	4.7224	
5ppb	2.888	4.7492	
5ppb	2.888	4.759	
5ppb	2.893	4.6863	

TableS2 The reproducibility detection results of snow sample

Sample	Retention time (min)	Concentration (ng /mL)	RSD
Snow sample 1	2.786	3.8646	10.5%
Snow sample 1	2.794	3.8597	
Snow sample 2	2.79	3.9561	
Snow sample 2	2.79	3.8483	
Snow sample 3	2.794	3.8994	
Snow sample 3	2.786	3.8592	