**Supporting Information for**

**A novel approach in sample preparation for analysis of Sb isotope ratios in**

**natural water by MC-ICP–MS**

## S1:  Typical operating conditions for the MC-ICP–MS

Table S1. Operating parameters for the HG-MC-ICPMS system.

| | |
| --- | --- |
| Hydride generator | Designed and manufactured by our research group |
| Mass spectrometer | Nu Plasma II MC-ICP–MS |
| Acid medium | HCl 3 M |
| Reducing agent medium | 0.5 wt% NaBH4 in 0.5 wt% NaOH |
| Sample or standard acidity | HCl 3 M |
| Cup configuration | L4(111), L3(112), L2(113), L1(114), Ax(115), |
| Cup mass | H3(118), |
| | H6(121), H7(123), H8(125) |
| Operating parameters Introduction system (Cd) | Aridus II with a 50 μL/min PFA nebulizer |
| RF power | 1300 W |
| Cooling Ar flow rate | 15.0 L min$^{-1}$ |
| Auxiliary Ar flow rate | 0.80 L min$^{-1}$ |
| Sample Ar flow rate | 0.06 L min$^{-1}$ (adjusted daily) |
| Nebulizer Ar flow rate | 20 PSI (adjusted daily) |
| Sweep gas flow rate in Aridus II | 1.8 L min$^{-1}$ (adjusted daily) |
| Analysis Number | 1 block of 50 cycles |
| Integration time | 10 s |

| Sample transfer time | 60 s |
|---|---|
| Sample washout time | 300 - 600 s |

## S2: Typical operating conditions for the AFS

Table S2. Operating parameters for the AFS system.

| | |
|---|---|
| Hydride generator | Designed and manufactured by our research group |
| Mass spectrometer | AFS |
| Acid medium | HCl 3 M |
| Reducing agent medium | 2 wt% $NaBH_4$ in 0.5 wt% NaOH |
| Sample or standard acidity | HCl 3 M |
| Lamp current | 60-70 m A |
| Negative high voltage of photomultiplier tube | 280-300 V |
| Measurement method | Standard curve method |
| Integration method | Peak area |
| Carrier gas flow | 400 ml/min |
| Shielding gas flow | 900-1000 ml/min |
| Atomizer preheating temperature | 200℃ |

## S3: Analysis method of dissolved organic matter (DOM) in natural water

As carbon is the skeleton element of DOM, its mass usually accounts for more than half of DOM, so the content of DOM is often characterized by the concentration of dissolved organic carbon (DOC).

Table S3. DOC concentration in different types of water

| Type | DOC concentration (mg $L^{-1}$) |
|---|---|
| Seawater | 0.5~1 |
| River | 5~9 |
| Oligotrophic lake | 2~3 |
| Eutrophic lakes | 9~16 |
| Soil seepage | 19~31 |
| Groundwater ($CaCO_3$ aquifer) | 0~1 |

Humic acids (HAs) are a type of macromolecular organic substance in nature, mainly from the sediments of soil, water and plant bodies that are decomposed by microorganisms. [1] The soluble organic matter in the overlying water of a eutrophic lake is dominated by soluble microbial metabolites and humic acid-like DOM, and as the degree of eutrophication increases, the proportion of humic acid-like DOM is higher. [1] By artificially adding humic acid to fit the humus in natural water, the recovery rate of the Sb standard solution with humic acid was measured under this method.

$UV_{254}$ represents the absorption value of organics, such as aromatic hydrocarbons in water, at a wavelength of 253.7 nm in the ultraviolet region. It indirectly represents the content of organics in the water and has good

correlation with chromaticity, etc. [2] The $UV_{254}$ value of unsaturated organic matter measured by ultraviolet spectrophotometry is stable and reliable, and $UV_{254}$ can reflect the content of unsaturated organic matter in water. [3]

Formula: KHP-OCconc.= $(UV_{254}-0.0018)/0.0144$

The calibration curve:

Table S4. The standard curve with KHP as the reference material

| UVA@254 nm (cm$^{-1}$) | KHP-SCS Preparation ORGANIC CARBON (mg L$^{-1}$) | OC-PDS (mL added per liter of LRW) |
|---|---|---|
| 0.0738 | 5 | 10 |
| 0.1458 | 10 | 20 |
| 0.2898 | 20 | 40 |
| 0.4338 | 30 | 60 |

The instrument for determining the content of organic matter is a UV-2900

Test reagent: potassium hydrogen phthalate (KHP)

Molecular formula: $C_8H_5KO_4$, Relative molecular weight: 204

The proportion of C: 47%

The above formula is the calculation of the content of C in KHP:

The concentration of KHP was 1 g L$^{-1}$, diluted to the appropriate concentration for calculation.

For absorption values, the measurement range of ultraviolet absorbance in general is 0.005~0.900 with the best accuracy.

## S4: The operation process of DOM measurement

(1) Water sample dilution: the sample shall be based on the optical path of the color pan, and the absorbance shall be generally guaranteed between 0.005~0.900. If it exceeds this range, the water sample shall be diluted with clean water containing no organic matter, so that the absorbance of the diluted water sample shall be within this range.

(2) Preparation of water samples: The collected and filtered water samples were classified for reserve, and MQ water was prepared as a blank sample for comparative analysis with water samples.

(3) Spectrophotometric determination: the wavelength was set at 254 nm but was set to zero when measuring the blank sample. Then, the KHP standard sample was analyzed with known absorbance to verify whether the spectrophotometer was well calibrated. Finally, the determination was started at room temperature. At least two groups of water samples were used as the standard sample.

## S5: Results of DOM measurement
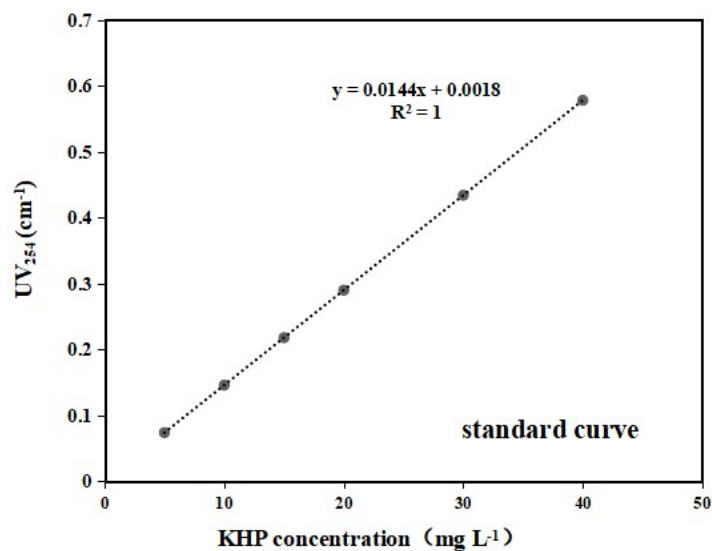
(1) The standard curve

Figure S1. The standard curve with KHP as the reference material

(2) Organic matter content of different samples

Table S5. Organic matter content of different samples

|  | Rice-field water | Rainwater | Lake water |
|---|---|---|---|
| DOM (mg $L^{-1}$) | 6.61 | 18.63 | 21.33 |
|  | 6.68 | 18.49 | 21.47 |
|  | 6.89 | 18.76 | 20.57 |
| Mean | 6.73 | 18.63 | 21.13 |
| 2 σ | 0.004 | 0.004 | 0.014 |

After the rice-field water, rainfall, and lake water were filtered through a 0.45 μm pore filter membrane, the soluble organic matter content in water samples from the rice field, Hongfeng Lake, and rainfall measured by $UV_{254}$ was $6.73 \pm 0.004$ mg $L^{-1}$, $18.63 \pm 0.004$ mg $L^{-1}$, and $21.13 \pm 0.014$ mg $L^{-1}$, respectively.

## S6: Preconcentration and purification of large volume (200 mL) lake water

Table S6. The preconcentration and purification experiments for a large volume (200 mL) of rice-field water, lake water and rainwater

| Type | Number of samples | Background value μg $L^{-1}$ | Standard sample content of Sb added ng | Measured value μg $L^{-1}$ | 2σ μg $L^{-1}$ | Recovery % | 2σ % |
|---|---|---|---|---|---|---|---|
| Rice-field water | 3 | – | 0 | 1.00 | 0.01 | – | – |
| lake water | 3 | – | 0 | 0.18 | 0.05 | – | – |
| rainfall | 3 | – | 0 | 0.04 | 0.02 | – | – |
| Rice-field water+std | 3 | 1.00 | 400 | 4.99 |  | 100.0 | 0.05 |
| lake water+std | 3 | 0.18 | 200 | 2.19 |  | 95.4 | 0.00 |

| rainfall+std | 3 | 0.04 | 50 | 0.51 | | 100.4 | 0.03 |

## S7: Sb isotope composition of different water samples

Table S7. Sb isotope composition of different water samples

| | Milli-Q water+Std | Volume (Milli-Q water) + Std | Lake water | Lake water+Std | Rice-field water | Rice field water+Std | Rainfall | Rainfall +Std |
|---|---|---|---|---|---|---|---|---|
| | -0.26 | -0.2 | 4.96 | 0.22 | 2.14 | 1.59 | 3.36 | -0.06 |
| | -0.32 | -0.1 | 4.87 | 0.28 | 2.88 | 1.27 | 2.79 | 0.27 |
| | -0.35 | 0.24 | 4.00 | 0.54 | 2.18 | 1.30 | 2.57 | -0.27 |
| | 0.26 | -0.1 | 4.55 | 0.44 | 2.20 | 1.19 | 2.80 | -0.30 |
| | 0.08 | 0.24 | 4.89 | | 2.43 | | 2.84 | |
| | 0.07 | -0.2 | 4.70 | | 2.70 | | | |
| | -0.24 | 0.17 | | | | | | |
| | -0.36 | -0.2 | | | | | | |
| | 0.02 | 0.12 | | | | | | |
| | -0.02 | | | | | | | |
| | -0.02 | | | | | | | |
| $(\varepsilon^{123}Sb)_M$ | 0.06 | | | | | | | |
| | 0.16 | | | | | | | |
| | -0.34 | | | | | | | |
| | 0.24 | | | | | | | |
| | 0.19 | | | | | | | |
| | 0.3 | | | | | | | |
| | 0.28 | | | | | | | |
| Mean | -0.01 | 0.00 | 4.66 | 0.37 | 2.42 | 1.34 | 2.87 | -0.09 |
| 2 σ | 0.48 | 0.39 | 0.71 | 0.29 | 0.62 | 0.35 | 0.58 | 0.52 |
| Sb(ng) | 20 | 20 | 4.8 | 24.8 | 31.2 | 51.2 | 1.8 | 20.54 |
| $(\varepsilon^{123}Sb)_T$ | | | - | 0.89 | - | 1.47 | - | 0.22 |

| $\triangle(\varepsilon^{123}Sb)$ | | - | -0.52 | - | 0.13 | - | 0.32 |

Std: Sb standard solution sample, $(\varepsilon^{123}Sb)_M$: measured Sb isotope composition, $(\varepsilon^{123}Sb)_T$: theoretical Sb isotope composition, σ: standard deviation, Mean: average value. The unit of antimony isotope composition is ε.

## S8: Sb isotope composition of artificial and natural humus with different gradients

Table S8. Sb isotope composition of artificial and natural humus with different gradients

| | Humus content (mg L⁻¹) | Artificial Humus | Artificial humus+Std | Natural humus | Natural humus+Std | 2σ |
|---|---|---|---|---|---|---|
| Sb(ng) | 5 | 0.23 | 20.23 | 0.72 | 20.72 | |
| | 10 | 0.01 | 20.01 | 0.94 | 20.94 | |
| | 15 | 0.06 | 20.06 | | | |
| | 20 | 0.14 | 20.14 | 1.48 | 21.48 | |
| $(\varepsilon^{123}Sb)_M$ | 5 | 2.28 | -0.02 | 3.89 | 0.60 | 0.41 |
| | 10 | 2.25 | -0.24 | 6.07 | 0.88 | |
| | 15 | 2.82 | -0.06 | | | |
| | 20 | 1.19 | 0.24 | 7.05 | 0.48 | |
| $(\varepsilon^{123}Sb)_T$ | 5 | | 0.11 | | 0.12 | |
| | 10 | | 0.08 | | 0.25 | |
| | 15 | | 0.09 | | | |
| | 20 | | 0.04 | | 0.46 | |
| $\triangle(\varepsilon^{123}sb)$ | 5 | | -0.14 | | 0.48 | |
| | 10 | | 0.33 | | 0.63 | |
| | 15 | | 0.16 | | | |
| | 20 | | 0.19 | | 0.02 | |

Std: Sb standard sample, $(\varepsilon^{123}Sb)_M$: measured Sb isotope composition, $(\varepsilon^{123}Sb)_T$: theoretical Sb isotope composition.

## S9: Blank correction of samples

The process blank of our experiment was homogeneous, which means that all of our vessels were washed under exactly the same conditions, as well as the same reagent and operation process. During our experiment, the process blank was monitored by using ultrapure water as the sample. To avoid the influence of blank on the isotope composition of the sample. If the blank is greater than 1%, we will conduct blank correction on the measured isotope of the sample. The correction formula is as follows:

$$(\varepsilon^{123}Sb)_{Sample} = [(\varepsilon^{123}Sb)_M - (\varepsilon^{123}Sb)_{Blank} \cdot (M_{Blank} / M_{(Sample+Blank)})]/(M_{Sample} / M_{(Sample+Blank)})$$

$(\varepsilon^{123}Sb)_M$: measured Sb isotope composition of samples, $(\varepsilon^{123}Sb)_{Blank}$: measured Sb isotope composition of blank, $M_{Sample}$: Mass of sample Sb, $M_{Sample}$: Mass of sample blank, $M_{(Sample+Blank)}$: Mass of sample Sb and blank Sb.

## SI REFERENCES

[1] Maccarthy P．(2001) The principles of humic substances: an intro-duction to the first principle．Soil Sci, 166: 738-751．

[2] Cihlar, Z., Vojtova, L., Michlovska, L. and Kucerik, J. (2016) Preparation and hydration characteristics of carbodiimide crosslinked lignite humic acids[J]. Geoderma, 2016,274:10-17.

[3] Yao, X., Zhang, YL., Zhu, GW., Qin, BQ., Feng LQ., Cai, LL., and Gao, GA. (2010) Resolving the variability of CDOM fluorescence to differentiate the sources and fate of DOM in Lake Taihu a nd its tributaries. Chemosphere, 82 (2) :145-155.