

Supporting Information

The role of free radicals/reactive oxygen species in MeHg photodegradation-importance of utilizing appropriate scavengers

Xiaoxiao Han[‡], Yanbin Li^{†,‡,*}, Dan Li[‡], and Chang Liu[‡]

[†]Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, Ocean University of China, Qingdao 266100, China

[‡]College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao 266100, China

*Corresponding Author:

Yanbin Li

Tel: +86-0532-66786355

Fax: +86-0532-66782301

Email address: liyanbin@ouc.edu.cn

This supporting information contains 16 pages, including 3 Figures and 6 Tables.

Determination of MeHg in water samples

MeHg in water samples was analyzed using distillation-aqueous ethylation derivatization-purge and trap followed by GC/CV-AFS detection. Acidified water samples were distilled according to the EPA method 1630. 45 mL distilled water was then poured into a 150 mL bubbler and the volume was brought to 100 mL with DI water. 2 mL of acetate buffer (2 M) and 50 μL of 1% NaBEt_4 were added and allowed to react for 15 min. Ethylation products were purged from the bubbler with N_2 at 200 mL min^{-1} for 15 min, and then trapped on a Tenax trap. The trap was dried for 5 min under 200 mL min^{-1} of N_2 . Finally, the trapped Hg species were thermally desorbed and separated using an OV-3 packed column at $70\text{ }^\circ\text{C}$ and then measured with a Model III AFS (Brooks Rand, USA).

Standard quality assurance and control procedures were followed during the analysis of MeHg. For each 20 samples, two method blanks and two spikes were included. The recoveries of all spikes (85–110%) were within the acceptable recoveries of the EPA method 1630 (65–135% for MeHg).

Determination of ancillary parameters in water samples

The concentration of dissolved organic carbon (DOC) was determined by a TOC analyzer (Analyticjena, Germany). Nitrate (NO_3^-) was determined by an Auto Analyzer 3 (SEAL Analytical, Germany). Total dissolved iron (Fe) in seawater and freshwater was measured by an adsorptive cathodic stripping votammetry (HMDE, Metro hmmodel 797 VA, Switzerland) and an ICP-AES (Thermo Fisher Inc., USA), respectively.¹ pH was measured by a pH meter (Sartorius Inc., Germany). Salinity was measured by a salinity meter (YK Lutron, China). Chloride (Cl^-) was measured by an ICS-2100 ion chromatography (Thermo Fisher, USA).

Determination and analysis of Excitation-emission matrix spectroscopy (EEMs) and UV-visible radiation absorbance spectra in natural water

EEMs were obtained using a Fluorolog 3 scanning fluorometer equipped with a 450W Xe arc lamp (Ushio Inc., Japan). The excitation wavelength was 240–480 nm (5 nm intervals), and the emission wavelength (Em) was 250–580 nm (5 nm intervals).² The integration time was set to be 0.05s.³ These spectra were normalized to quinine sulfate units using 0.01 mg L^{-1} quinine sulfate monohydrate prepared in $0.05\text{ mol L}^{-1}\text{ H}_2\text{SO}_4$.³⁻⁵ The Rayleigh and Raman scattering was corrected for by subtracting normalized DI water. PARAFAC modeling was

performed for all measured EEMs of water samples from Laoshan Reservoir, Ink River and Stone Old Beach. 3 components were modeled for these data, including two humic-like peaks (C1 (Ex/Em 330/415 nm) and C2 (Ex/Em 370/460 nm)) and one protein-like peak (C3 (Ex/Em 295/340 nm)).⁶ C1 is thought to be terrestrial humus and it commonly exists in river and coastal water. C2 is related to the DOM with high molecular weight and strong aromaticity, while C3 is related to DOM influenced by human activity and sewage disposal.^{6,7} The total fluorescence intensity (TFI) was calculated by the sum of the 3 components.⁷

Humification index (HIX) and biotic index (BIX) are two indices that can represent the properties and source of DOM. HIX was calculated by dividing the area under the emission spectra at 435–480 nm by that at 300–345 nm at an excitation wavelength of 255 nm. Higher HIX values indicate the higher humification degree of CDOM, meaning that the DOM is more stable and mature.³ BIX was calculated as the ratio of emission fluorescence intensities at 380 nm to that at 430 nm with an excitation wavelength of 310 nm. Higher BIX represents that more CDOM is from biological source, e.g., microbial originated compounds.⁷

The UV-visible radiation absorbance spectrum of water samples from Laoshan Reservoir, Ink river and Stone Old Beach at the wavelength of sunlight (280-700 nm) were measured using a UV-2550 ultraviolet (UV)-visible spectrophotometer (SHIMADZU, Japan). $SUVA_{254}$ was calculated by dividing the radiation absorbance at 254 nm by DOC concentrations.^{5, 8}

Calculation of the pH of scavengers in DI water

For weak monoacid solution, the concentration of H^+ in scavenger HA solution can be described as Eq. (1).^{9, 10} Since $K_a C \geq 20K_w$, Eq.(1) can be simplified to Eq.(2).¹⁰

$$[H^+]^3 + K_a[H^+]^2 + (K_a C + K_w)[H^+] - K_a K_w = 0 \quad (1)$$

$$[H^+]^2 + K_a[H^+] - K_a C = 0 \quad (2)$$

where K_a is the dissociation constant of scavenger HA; K_w is the dissociation constant of water (1×10^{-14} in this study); C is the added concentration of HA. By resolving Eq. (2), pH of scavenger HA solution can be calculated by Eq. (3).

$$pH = -\lg [H^+] = -\lg \frac{-K_a + \sqrt{K_a^2 + 4K_a C}}{2} \quad (3)$$

Then, the change in the pH of DI water after the addition of various concentrations of

monoacidic scavengers can be calculated by Eq. (4).

$$|\Delta pH| = |pH(\text{scavenger}) - pH(\text{DI water})| = -\lg \sqrt{K_w} + \lg \frac{-K_a + \sqrt{K_a^2 + 4K_a C}}{2} \quad (4)$$

If the scavenger is weak monobasic, the pH can be described as Eq. (5) and ΔpH can then be calculated by Eq. (6).

$$pH = -\lg K_w - pOH = -\lg K_w + \lg [OH^-] = -\lg K_w + \lg \frac{-K_b + \sqrt{K_b^2 + 4K_b C}}{2} \quad (5)$$

$$\begin{aligned} |\Delta pH| &= |pH(\text{scavenger}) - pH(\text{DI water})| = (-\lg K_w + \lg \frac{-K_b + \sqrt{K_b^2 + 4K_b C}}{2}) + \lg \sqrt{K_w} \\ &= -\lg \sqrt{K_w} + \lg \frac{-K_b + \sqrt{K_b^2 + 4K_b C}}{2} \end{aligned} \quad (6)$$

where K_b is the dissociation constant of monobasic scavenger.

Calculation of the speciation of MeHg in the presence of scavengers and DOM

The species of MeHg in scavenger solutions include MeHg^+ , MeHgOH , MeHg-DOM , and MeHg complexed with scavengers (MeHgLc). Then, the total concentration of MeHg can be described as Eq. (7)

$$[\text{MeHg}]_{\text{total}} = [\text{MeHg}^+] + [\text{MeHgOH}] + [\text{MeHgDOM}] + [\text{MeHgLc}] \quad (7)$$

Formation and dissociation of the relevant species are listed as Eq. (8) - (10).



By resolving Eqs. (8) - (10), the percentage of MeHg-DOM without the addition of scavenger (P_{control}) can be described as Eq. (11), while the percentage of MeHg-DOM in the presence of Lc scavenger ($P_{\text{scavenger}}$) can be described as Eq. (12). Then, the effects of scavenger on MeHg-DOM complexation ($P_{\text{scavenger}}/P_{\text{control}}$) can be calculated by Eq. (13).

$$P_{\text{control}} = \frac{K_{\text{MeHgDOM}}[\text{DOM}]}{1 + K_{\text{MeHgDOM}}[\text{DOM}] + K_{\text{MeHgOH}}[\text{OH}^-]} \quad (11)$$

$$P_{\text{scavenger}} = \frac{K_{\text{MeHgDOM}}[\text{DOM}]}{1 + K_{\text{MeHgDOM}}[\text{DOM}] + K_{\text{MeHgOH}}[\text{OH}^-] + K_{\text{MeHgLc}}[\text{Lc}]} \quad (12)$$

$$P_{\text{scavenger}}/P_{\text{control}} = \frac{1 + K_{\text{MeHgDOM}}[\text{DOM}] + K_{\text{MeHgOH}}[\text{OH}^-]^*}{1 + K_{\text{MeHgDOM}}[\text{DOM}] + K_{\text{MeHgOH}}[\text{OH}^-] + K_{\text{MeHgLc}}[\text{Lc}]} \quad (13)$$

where $[\text{OH}^-]^*$ is the concentration of OH^- in DOM solutions without scavengers.

As $K_{\text{MeHgDOM}}[\text{DOM}] \gg K_{\text{MeHgOH}}[\text{OH}^-]$ and $K_{\text{MeHgOH}}[\text{OH}^-]^*$ at the experimental pH range of 2-10 (the following parameter values were adopted for the estimation: $\log K_{\text{MeHgDOM}} = 11$ (related to DOM unit, mmol C L^{-1})¹¹, $\log K_{\text{MeHgOH}} = 9.3$ ¹²⁻¹⁴, $[\text{DOM}] = 0.83 \text{ mmol C L}^{-1}$) and K_{MeHgLc} , K_{MeHgDOM} and $[\text{DOM}]$ are constants, Eq. (13) can then be simplified to Eq. (14).

$$P_{\text{scavenger}}/P_{\text{control}} = \frac{1}{1 + b[\text{Lc}]} = \frac{1}{1 + bC} \quad (14)$$

where b is a constant refers to the relation of MeHg complexed with DOM to scavenger concentrations; C is the concentration of a certain scavenger (mmol L^{-1}).

Effects of the candidate FR/ROS scavengers on the complexation of MeHg with DOM in nature waters

The possible effects of candidate scavengers on MeHg-DOM complexation in three tested natural waters were tested by ultrafiltration centrifugation with a 3 kDa centrifugal filter (Sartorius). Scavengers were added into 50 ml filtered water (0.22 μm cellulose acetate filter) containing 10 ng L^{-1} MeHg to form a final concentration of 1 mmol L^{-1} and/or 10 mmol L^{-1} . A trial without adding any scavenger was employed as a control. After equilibrating for 24 h, 10 mL solutions were ultrafiltered using a 3 kDa centrifugal filter (Sartorius) at 6000 rpm for 25 min. MeHg concentrations in the two fractions ($>3 \text{ kDa}$ and $<3 \text{ kDa}$) were analyzed, and the percentage of MeHg complexed with $>3 \text{ kDa}$ DOM (P) were calculated according to Eq. (15). Triplicates were employed for each trial. P values with and without the addition of a certain scavengers were compared to evaluate if the scavenger affects the complexation of MeHg with DOM.

$$P = \frac{(C_1 - C_2) \times V_1}{C_1 \times V_1 + C_2 \times V_2} \quad (15)$$

where C_1 and C_2 are the concentrations of MeHg in the residual and filtrate solutions, respectively. V_1 and V_2 are the volumes of residual and filtrates solutions in the centrifugal tubing.

The effect of SOD on the complexation of MeHg with DOM was tested by a 10 kDa Ultra-15 centrifugal filter. SOD was added to 50 ml filtered water containing 10 ng L^{-1} MeHg to form a final concentration of 0.1 and 10 mg L^{-1} . After equilibrating for 24 h, 10 mL solution was ultrafiltrated using a 10 kDa centrifugal filter at 5000 rpm for 15 min. MeHg in the filtrate and residual solutions were determined. $(1-P)$ values with and without the addition of SOD were calculated to test the influence of SOD on MeHg-DOM complexation in the three tested natural waters.

Figure S1 Variation of MeHg concentrations in 10 mmol L⁻¹ scavenger solutions (β -carotene was 1 mmol L⁻¹ and SOD was 10 mg L⁻¹) with time during incubating under sunlight (A) and in the dark (B) for 3 days.

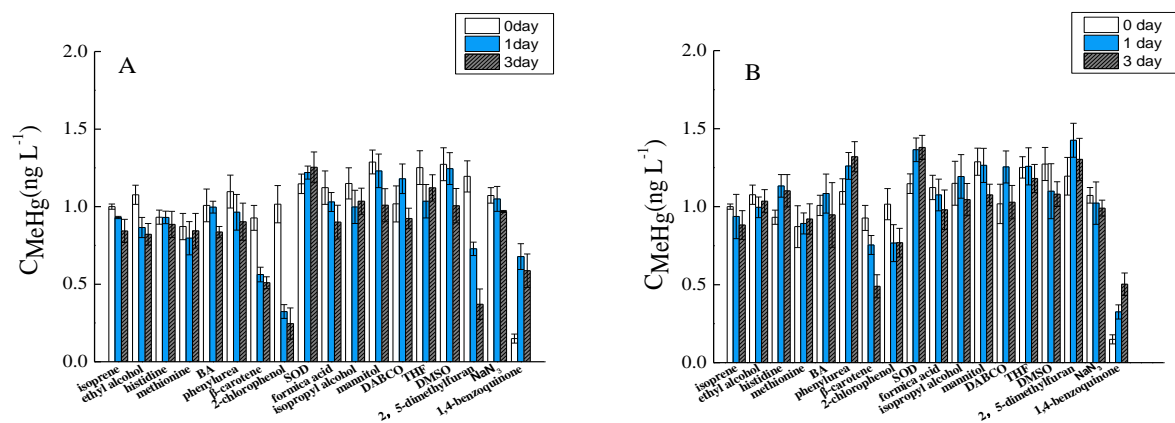


Figure S2 Variation of MeHg concentrations in natural water with and without the addition of scavengers with time during incubating under sunlight for 3 days. A, Stone Old Beach. B, Ink River. C, Laoshan Reservoir.

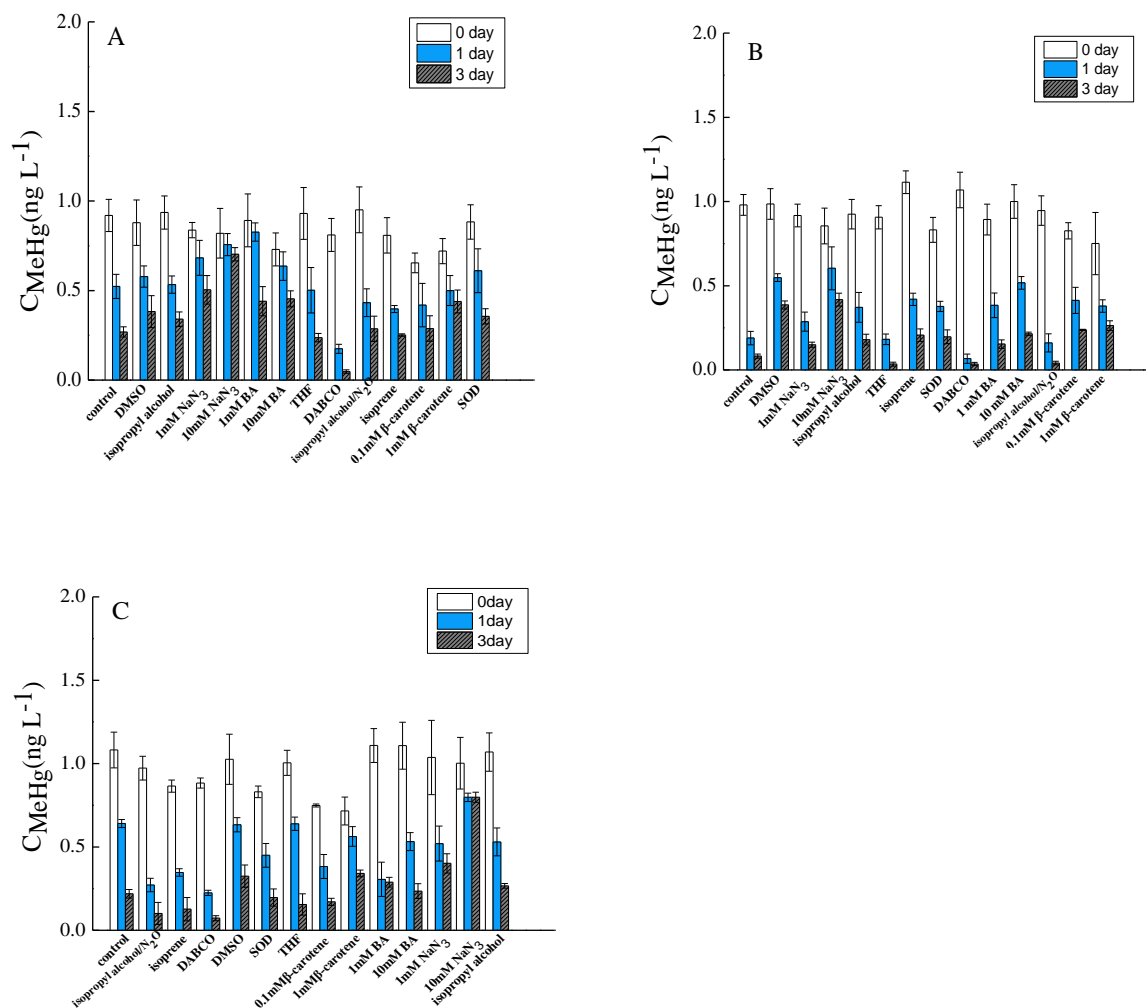


Figure S3 The EEMs of the three components of DOM in water of Laoshan Reservoir, Ink River and Stone Old Beach. C1 and C2 are humic-like substances and C3 is the protein-like substance.

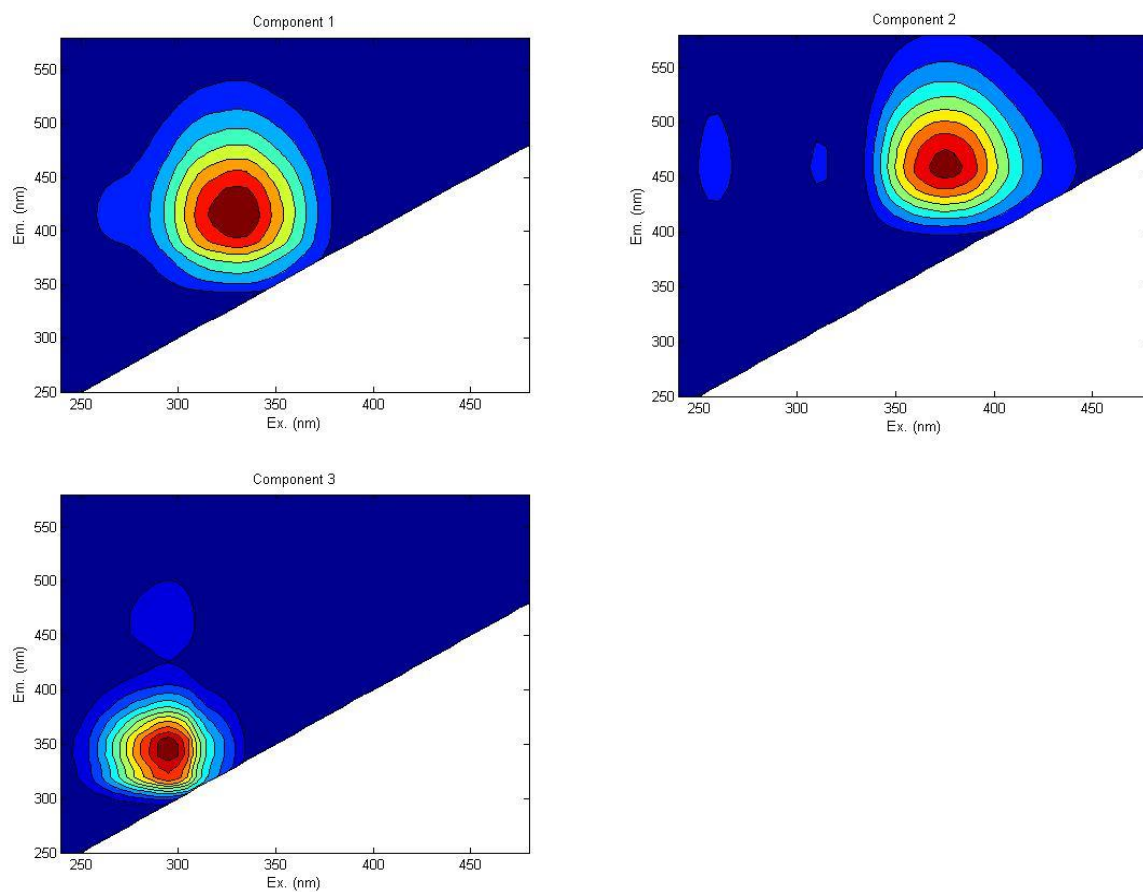


Table S1 Chemical characteristics of three tested natural waters. HIX, humification index.

BIX, biological index. FI, fluorescence intensity. TFI, total fluorescence intensity.

BIX in Ink River was around 0.8, indicating that DOM in this system may be mainly from terrestrial discharge.^{3, 15} A >1.0 BIX was observed in Laoshan Reservoir, suggesting the dominant contribution of biological origin to DOM.¹⁴ Both terrestrial discharge and biological origin are the important sources of DOM in Stone Old Beach, indicated by its BIX value (in the range of 0.8-1.0). The percentage of C3 to TFI in Ink River was much higher than that in the other two systems, indicating that a large proportion of DOM in Ink River is from sewage discharge. In addition, the humification of DOM in Ink River was the lowest among the three tested waters, indicated by its low HIX values. Since the activity of DOM was thought to become weaker with increasing humification,^{3, 16} DOM in Ink River may be more photoactive than the other two systems.

Parameters	Laoshan Reservoir	Stone Old Beach	Ink River
pH	8.21±0.07	7.90±0.01	8.11±0.04
Salinity, ‰	0.05±0.05	26.6±0.6	1.7±0.2
Cl ⁻ , mol L ⁻¹	(0.48±0.11)×10 ⁻³	0.48±0.02	(6.74±0.31)×10 ⁻³
NO ₃ ⁻ , μmol L ⁻¹	87.12±8.13	0.61±0.10	156.30±4.29
DOC, mg L ⁻¹	5.12±0.04	3.35±0.27	6.97±0.75
Fe, nmol L ⁻¹	61.3±2.3	7.1±0.5	132.0±6.8
HIX	7.46	2.44	1.98
BIX	1.14	0.97	0.81
FI of C1(humic-like)	2.14	0.30	5.94
FI of C2(humic-like)	1.67	0.29	4.93
FI of C3(protein-like)	0.31	0.20	9.89
TFI	4.12	0.79	20.76
SUVA ₂₅₄ , L mg ⁻¹ m ⁻¹	1.7	0.5	2.8

Table S2 The scavengers used in investigating MeHg photodegradation in natural water. DMSO, dimethylsulfoxide; BA, benzoic acid; DABCO, 1, 4-diazobicyclo(2, 2, 2)octane; THF, tetrahydrofuran; SOD, superoxide dismutase.

Scavengers	Concentration, mmol L ⁻¹	Description
N ₂ purging	Saturated nitrogen	
O ₂ purging	Saturated oxygen	
DMSO	10	Scavengers of •OH
isopropyl alcohol	10	Scavengers of •OH
BA	1,10	Scavengers of •OH
isoprene	10	Scavengers of ³ DOM*
N ₂ O/ isopropyl	Saturated N ₂ O,10	Scavengers of e ⁻ _{aq}
alcohol	1,10	Scavengers of ¹ O ₂
NaN ₃	10	Scavengers of ¹ O ₂
DABCO	0.1,1	Scavengers of ¹ O ₂
β-carotene	10	Scavengers of ¹ O ₂
THF		
SOD	10 mg L ⁻¹ , 0.1mg L ⁻¹	Scavengers of O ₂ ^{-•}

Table S3 Values of constants related to effects of scavengers on light transmittance, pH and MeHg-DOM complexation. a, the radiation absorbance constant of a certain scavenger. $pK_a = -\lg K_a$ and K_a is the acid dissociation constant of scavenger in DI water. b, a constant refers to the relation of the percentage of MeHg complexed with DOM with scavenger concentrations. DABCO, 1, 4-diazobicyclo (2, 2, 2) octane. BA, benzoic acid.

Scavengers	pK_a^*	a (UVB)	r^2	a (UVA)	r^2	a (PAR)	r^2	b	r^2
formic acid	3.74								
DABCO	8.82								
histidine	6.0,1.82,9.17							0.0077	0.97
methionine	2.28,9.21							0.031	0.91
NaN_3	5.09 ^c							0.012	0.95
2,5-dimethylfuran		0.0048	0.98					0.0038	0.65
BA	4.21	0.010	0.65					0.011	0.75
2-chlorophenol	8.48	0.032	0.58						
phenylurea	13.82	0.27	0.75	0.0085	0.98				
β -carotene		3.8	0.98	3.7	0.98	4.4	0.97		
1,4-benzoquinone		0.42	0.99	0.065	0.99	0.017	0.95		
ethyl alcohol	16.00								
isopropyl alcohol	16.50								
mannitol	12.59 ^c								

*the pK_a of scavengers were cited from Evans pK_a table.

^c the pK_a of scavengers were calculated by ChemAxon.

Table S4 Recovery of MeHg in different concentrations of 1, 4-benzoquinone solutions.

MeHg was added to 0.01 and 0.1 mmol L⁻¹ of 1, 4-benzoquinone solution (prepared in DI water) to form a final concentration of 1 ng L⁻¹. MeHg in the solution was then determined using the aqueous ethylation derivatization-purge and trap-GC/CVAFS method without distillation.

Concentration (mmol L ⁻¹)	Recovery of MeHg (%)
0.1	7.7 ±1.0
0.01	85.0 ±9.3

Table S5 Recovery of MeHg in the presence of 1 mmol L⁻¹ β -carotene after being incubated under sunlight or in the dark for 0-3 days.

A certain amount of β -carotene was added to 100 mL phosphate solutions (10 mmol L⁻¹) in a quartz bottle to form a final concentration of 1 mmol L⁻¹. The bottles were incubated under sunlight or in the dark for 0-3 days. MeHg was added to the β -carotene solutions after incubating for 0, 1, 3 days to form a final concentration of 1 ng L⁻¹ and equilibrated for 30 min. Then MeHg in the solution was measured by using distillation-aqueous ethylation derivatization-purge and trap-GC/CVAFS method. A good recovery of MeHg was observed in freshly prepared β -carotene solution. However, β -carotene was found to significantly affect the analysis of MeHg after incubating for >1 days and the effect became more pronounced with increasing incubation time.

Incubation time	Recovery of MeHg (%)	
	light	dark
0 day	92.3 \pm 3.6	92.3 \pm 3.6
1 day	62.7 \pm 4.2	70.7 \pm 5.2
3 day	49.9 \pm 4.7	58.1 \pm 3.7

Table S6 The influence of scavengers on water chemical characteristics in nature waters. LR, Laoshan Reservoir; IR, Ink River; SOB, Stone Old Beach. BA, benzoic acid; DABCO, 1, 4-diazobicyclo (2, 2, 2) octane; DMSO, dimethylsulphoxide; THF, tetrahydrofuran; SOD, superoxide dismutase.

Scavengers	pH		Irradiance transmittance							Percentage of MeHg complexed with DOM (%)			Analysis of MeHg (recovery, %)		
	LR	IR	SOB	UVB-LR	UVB-IR	UVB-SOB	UVA-LR	UVA-IR	UVA-SOB	LR	IR	SOB	LR	IR	SOB
control	8.21	8.11	7.90	100.0	100.0	100.0	100.0	100.0	100.0	89.5±1.2	84.6±1.9	80.1±2.4	100.0	100.0	100.0
BA (1mmol L ⁻¹)	6.71	6.62	6.93	98.0	98.2	97.2	100.6	98.5	100.4	/	/	/	94.3±5.3	90.2±3.8	92.5±4.6
BA (10 mmol L ⁻¹)	3.63	3.42	3.94	69.9	75.9	69.4	100.6	105.0	100.5	/	/	/	94.3±4.9	80.3±4.3	73.7±3.2
NaN ₃ (1 mmol L ⁻¹)	8.24	8.13	7.95	100.4	101.4	100	100.3	100.5	100.0	56.9±1.8	61.4±2.8	55.1±2.2	89.3±4.6	93.6±6.8	92.8±5.1
NaN ₃ (10 mmol L ⁻¹)	8.35	8.27	7.99	100.6	104.5	98.9	100.5	99.6	99.0	19.7±1.3	40.7±1.9	37.8±3.2	85.6±5.7	92.1±5.4	80.9±4.1
β-carotene (0.1 mmol L ⁻¹)	7.88	7.83	7.72	39.2	62.1	71.3	44.00	73.6	77.2	/	/	/	83.5±5.4	85.2±3.5	80.3±4.3
β-carotene (1 mmol L ⁻¹)	8.05	8.12	7.85	6.2	5.7	57.1	5.8	4.8	58.7	/	/	/	76.9±4.6	84.7±4.5	75.8±3.4
DABCO	9.52	9.43	9.37	100.9	103.4	100.8	100.6	105.6	100.6	/	/	/	91.6±6.6	92.1±4.9	91.7±5.6
SOD(10 mg L ⁻¹)	8.16	8.10	7.96	102.5	92.3	98.7	101.7	96.6	99.3	58.8±3.1	21.7±1.8	14.8±0.7	90.4±5.4	93.5±5.7	95.4±3.2
SOD(0.1 mg L ⁻¹)	8.18	8.17	7.93	101.5	100.5	100.7	100.3	101.6	100.9	96.0±0.5	88.2±3.3	79.0±0.7	93.4±0.5	99.6±9.4	92.5±1.5
DMSO	8.12	8.06	7.94	100.6	100.5	99.8	100.4	100.8	99.8	37.4±2.0	44.4±3.0	66.1±3.2	96.0±3.5	90.5±5.2	100.2±3.9
isopropyl alcohol	8.22	7.91	7.93	101.0	101.6	100.1	100.7	98.7	100.0	89.3±4.5	83.1±0.5	80.5±2.6	91.0±4.6	94.3±5.9	94.1±3.6
THF	8.24	8.05	7.94	101.2	100.6	100.3	100.5	99.2	100.2	90.4±2.1	82.4±3.3	81.7±2.3	90.3±5.3	92.5±4.0	100.5±5.7
isoprene	8.27	8.07	7.81	100.9	100.8	100.6	100.9	102.1	100.6	89.0±3.0	82.6±2.1	81.2±2.3	88.3±4.1	105±4.3	91.2±8.4
N ₂ O/isopropyl alcohol	8.41	8.52	8.05	101.2	101.3	101.1	100.8	104.4	100.9	89.3±4.5	83.1±0.5	80.5±2.6	105.2±2.5	100.5±4.2	90.3±4.3

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