Effects of Oxygenation Resuspension on DOM Composition and Its Role in Reducing Dissolved Manganese in Drinking Water Reservoirs

Supporting Information

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Summary: 25 pages, 12 figures and 6 tables.

Sediment resuspension experiments were conducted in six drinking water source reservoirs located in Zhejiang Province, China, designated as Reservoirs A, B, C, D, E, and F (Fig. S1). Reservoir F was identified to have a relatively higher manganese content in its sediments and was therefore selected as the source for sediment samples used in laboratory simulation experiments. To protect the confidentiality of the reservoirs, all reservoir names have been anonymized and represented using letter codes.

Specific sediment resuspension procedures were applied are: Reservoir A (5 days), Reservoir B (21 days), Reservoir C (39 days), Reservoir D (14 days), Reservoir E (11 days) and Reservoir F (29 days). For reservoir F, water and sediment samples were analyzed to evaluate the impact of sediment resuspension on Mn release and its control.



Fig. S1: Sediment resuspension study in six reservoirs and laboratory simulation using high-manganese sediment from Reservoir F

A pre-experiment was conducted to determine the optimal solid-liquid ratio for the sediment-water mixture in the simulation system. Different solid-liquid ratios (20, 30, 40, 50, 60, 70 g L⁻¹) were tested to evaluate metal ion release. The solid-liquid ratio of 40 g L⁻¹ was selected for the simulation system based on the release fraction, which was determined by comparing the final concentrations at 48 hours with the initial concentrations at 0.3 hours, when the maximum aqueous concentrations were observed.

The figure illustrates the maximum release amounts of metals at various solid-liquid ratios in the sediment from Reservoir F. Samples were placed in a constant-temperature water bath shaker at 20°C with a shaking frequency of 260 r min⁻¹. Samples were collected at two time points: after 0.3 hours (early release concentration) and after 48 hours (equilibrium concentration). The maximum release amount was calculated as the difference between these two concentrations. The supernatant was then extracted by centrifugation at 3200 r min⁻¹, and metal concentrations were measured after filtration through a 0.45 µm membrane.



Fig. S2: Maximum release amounts of metals at different solid-liquid ratios in the sediment of Reservoir F. Samples were shaken in a constant temperature water bath at 20°C with a shaking frequency of 260 r min⁻¹, and metal concentrations were measured at early release (0.3 h) and equilibrium (48 h). The difference between these two time points represents the maximum release amount. The supernatant was extracted by centrifugation at 3200 r min⁻¹ and filtered through a 0.45 µm membrane.



Fig. S3: Monitoring of dissolved oxygen (DO), pH, and oxidation-reduction potential (ORP) before and after system startup

In this study, sediment collected from Reservoir F was used for laboratory simulation experiments. A schematic diagram of the simulation system is shown in Fig. S4. Each system consisted of a sealed black polyethylene buckets connected to an external aeration system to regulate dissolved oxygen (DO) levels by introducing either nitrogen or oxygen gas. Additionally, a stirring module was included to simulate sediment disturbance.

A total of 10 systems were set up: 8 systems with both aeration and stirring, each adjusted to DO levels of 0, 2, 5, and 7 mg L^{-1} , with two replicates per condition. Furthermore, one system was set up with aeration (DO level of 7 mg L^{-1}) but without stirring, and another served as a control system with neither aeration nor stirring.



Fig. S4: Schematic diagram of the simulation system



Fig. S5: Adsorption-desorption curves of the sediment in Reservoir F



Fig. S6: Comparison of colloidal manganese (colloid Mn) concentrations under different dissolved oxygen levels in simulation systems with stirring and no stirring conditions.

The composition and structural characteristics of DOM in overlying water were characterized using three-dimensional fluorescence spectroscopy. Parallel factor analysis (PARAFAC) modeling was conducted using the DOM Fluor toolbox in MATLAB 2022b. After removing Raman and Rayleigh–Tyndell scattering effects, outliers were identified and excluded based on leverage and loading plots. PARAFAC models with varying numbers of components were established, and a binary validation approach was applied to identify the optimal model.

Fluorescence datasets were compared using the OpenFluor online platform, where components were considered to have strong matching if the Tucker congruence coefficients (θ) for both excitation and emission spectra exceeded 0.95¹. The final model identified three components: C1, C2, and C3.

- **Component C1** (Ex = 225 nm, Em = 325 nm): Identified as protein-like matter, primarily associated with degraded proteins, particularly tryptophan-like compounds².
- Component C2 (Ex = 230 nm, Em = 415 nm): Representing terrestrial humic-like substances, characterized by aromatic structures, large molecular size³, and significant hydrophobicity^{4,5}.
- **Component C3** (Ex = 263 nm, Em = 464 nm):Corresponding to terrestrially derived terrestrial humic-like substances⁶, it is highly likely to befulvic acid-like substances^{7,8}.

The DOM-EEM spectra of the water samples were analyzed using Parallel Factor Analysis (PARAFAC), which mathematically decomposes the data into different fluorescence components with distinct spectral characteristics.



Fig. S7: Fluorescence component spectra of dissolved organic matter (DOM) in water. EEM data were analyzed using Parallel Factor Analysis (PARAFAC), which mathematically deconvoluted the spectra into distinct fluorescence components with independent spectral characteristics.



Fig. S8: Relationship between DOM components and dissolved oxygen (DO). (A) Effect of DO on the fluorescence intensity of component C1. (B) Correlation between the fluorescence intensity of C1 and Mn (II) concentration.



Fig. S9: Impact of sediment resuspension on Fe ion concentrations in the water column, based on practical tests conducted across six water source reservoirs (Reservoirs A-F)

Fig. SIO

In each simulation system, changes in manganese concentrations in the water were continuously monitored. Dissolved manganese (dissolved Mn) was determined by filtering water samples through a 0.22 μ m filter. Colloidal manganese (colloid Mn) was calculated as the manganese content in water filtered through a 1 μ m filter, subtracting the corresponding dissolved Mn. The first two panels represent systems without stirring at DO levels of 0 mg L⁻¹ and 7 mg L⁻¹. The subsequent four panels show systems with stirring at DO levels of 0, 2, 5, and 7 mg L⁻¹.



Fig. S10: Changes in dissolved and colloidal manganese concentrations in simulation systems. Dissolved Mn was measured after filtering water samples through a 0.22 μ m filter, while colloid Mn was calculated as the difference between manganese concentrations in 1 μ m-filtered and 0.22 μ m-filtered samples. The first two panels represent no-stirring systems with DO levels of 0 mg L⁻¹ and 7 mg L⁻¹, while the last four panels correspond to stirring systems with DO levels of 0, 2, 5, and 7 mg L⁻¹.

Fig. SII



Fig. S11: Dissolved organic carbon (DOC) concentrations in the simulators under varying dissolved oxygen (DO) levels (0, 2, 5, and 7 mg L^{-1}) (A); The relationship between DOC concentrations and manganese (Mn (II)) concentrations in the systems (B)



Fig. S12: Correlations between fluorescence components C2 and C3 and various metals, including Al, Ba, Fe, Mg, Sr, and Zn.

The sediment from Reservoir F exhibits several key physical and chemical properties. The moisture content, as per the standard HJ 613-2011, is 78.46%. The granularity distribution shows that the sediment particles have a Dx(10) of 3.87 μ m, a Dx(50) of 122.33 μ m, and a Dx(90) of 271.33 μ m, indicating a mixture of fine and coarse particles. In terms of sequential extraction of phosphorus, the following values were observed: Ex-IP (0.62145 mg L⁻¹), Fe-IP (2.01584 mg L⁻¹), Al-IP (0.62654 mg L⁻¹), Ca-IP (0.26148 mg L⁻¹), and Re-IP (0.10972 mg L⁻¹). The sediment also has a specific surface area of 23.3095 m² g⁻¹ as determined by BET analysis, with a pore volume of 0.08428 cm³ g⁻¹, measured using BJH adsorption. The average pore diameter is 17.0244 nm, indicating the presence of relatively fine pores in the sediment. These properties highlight the physical and chemical characteristics of the sediment, which are essential for understanding its behavior in environmental simulations.

| Parameters | Values | | | |
|-----------------------|---------------------------------------|--|--|--|
| Moisture content | | | | |
| HJ 613-2011 | 78.46% | | | |
| Granularity | | | | |
| Dx (10) | 3.87 | | | |
| Dx (50) | 122.33 | | | |
| Dx (90) | 271.33 | | | |
| Sequential extrac | tion of P | | | |
| Ex-IP | 0.6215 mg L ⁻¹ | | | |
| Fe-IP | 2.0158 mg L ⁻¹ | | | |
| Al-IP | 0.6265 mg L ⁻¹ | | | |
| Ca-IP | 0.2615 mg L ⁻¹ | | | |
| Re-IP | 0.1097 mg L ⁻¹ | | | |
| Surface Area | | | | |
| BET | 23.31 m ² g ⁻¹ | | | |
| Pore Volume | | | | |
| BJH Adsorption | $0.08428 \text{ cm}^2 \text{ g}^{-1}$ | | | |
| Pore diameter | | | | |
| BJH Adsorption | 17.02 nm | | | |

Table S1: Properties of sediment in Reservoir F

The extraction of various phosphorus (P) fractions was accomplished through a combination of the methodology proposed by ref.⁹, as subsequently refined by ref.¹⁰, and the phosphorus extraction protocol detailed by ref.¹¹. The determination of phosphorus refers to the ammonium molybdate spectrophotometric method¹².

Fraction Extraction method

| Ex-IP | 0.50 g sediment was mixed with 25 mL of 0.46 M NaCl, shaken for 1 hour, and centrifuged at 3000 rpm for 10 min. The supernatant was combined with a 10 mL rinse of extraction solution, filtered through a 0.45 μm membrane, and a 10 mL aliquot was transferred to a 25 mL tube. After adjusting pH to neutral with phenolphthalein, 0.5 mL of 10% ascorbic acid and 1 mL of molybdate solution were added, and the volume was brought to 25 mL with distilled water. Absorbance was measured at 700 nm after 15 min |
|-------|--|
| Fe-IP | Residue from Ex-IP was extracted with 25 mL of BD solution (0.11 M NaHCO ₃ + 0.11 M Na ₂ S ₂ O ₄) at 40°C for 0.5 hours, centrifuged, and combined with a 10 mL rinse. The mixture was filtered (0.45 μ m), and the measurement steps followed Ex-IP. |
| Al-IP | Residue from Fe-IP was extracted with 25 mL of 1 M NaOH at 25°C for 16 hours, centrifuged, combined with a 10 mL rinse, and filtered (0.45 µm). Measurement steps followed Ex-IP. |
| Ca-IP | Residue from Al-IP was extracted with 25 mL of 0.5 M HCl at 25°C for 16 hours, centrifuged, combined with a 10 mL rinse, and filtered (0.45 µm). Measurement steps followed Ex-IP. |
| Re-IP | Residue from Ca-IP was extracted with 25 mL of 1 M NaOH at 85°C for 24 hours, centrifuged, combined with a 10 mL rinse, and filtered (0.45 µm). Measurement steps followed Ex-IP. |

Table S2: Extraction methods and procedures for determining phosphorus fractions in Reservoir F sediment

| Reservoir | Month | Depth (m) | Water temperature (°C) | pН |
|-----------|-----------|-----------|------------------------|------|
| A | May - Jun | 10.12 | 21.89 | 9.55 |
| В | May - Jun | 11.18 | 29.28 | 8.38 |
| С | Apr - May | 20.62 | 20.33 | 9.98 |
| D | Aug - Sep | 8.36 | 30.70 | 8.46 |
| E | Oct | 3.95 | 19.40 | 8.80 |
| F | Oct - Nov | 6.97 | 18.80 | 7.70 |

Table S3: Basic information of the reservoirs used in field applications.

In systems with different dissolved oxygen levels, manganese concentrations in the water peaked within 15–30 minutes of stirring and then declined rapidly. The decline process was well described by a second-order kinetic equation: $1/c_t = 1/c_0 + k \cdot t$, where c_0 represents the modeled maximum Mn concentration, and k is the second-order rate constant. Table S4 presents the parameters of the second-order kinetic model and the results of statistical tests for each system.

| Operation | DO (mg L ⁻¹) | $c_{0} (\mu g L^{-1})$ | <i>k</i> (min ⁻¹) | <i>p</i> -value |
|-----------|--------------------------|--------------------------|-------------------------------|-----------------|
| Stir | 0 | 1.28 × 10 ³ | 1.31×10^{-5} | 0.0840 |
| Stir | 2 | 9.79×10^{2} | 5.14×10^{-5} | 0.0002 |
| Stir | 5 | 6.17×10^{2} | 5.75×10^{-4} | 0.0037 |
| Stir | 7 | 4.73×10^{2} | 2.57×10^{-5} | 0.0144 |

Table S4: Parameters of the second-order kinetic model and statistical test results for manganese concentration decline in systems with different dissolved oxygen levels.

For manganese (Mn) fractionation, the sequential extraction procedure outlined in the Chinese national standard¹³ was used. Extracted solutions were stabilized with 1% nitric acid and analyzed for manganese concentrations using inductively coupled plasma mass spectrometry (ThermoFisher iCAP Q).

This study primarily focused on the transformation relationships among three manganese fractions due to the relative stability of the residual fraction, which is less reactive chemically:

- **Mild acid-soluble fraction**: Elements electrostatically adsorbed on particle surfaces, released via ion exchange, or bound within carbonates.
- Reducible fraction: Elements associated with iron and manganese oxides.
- **Oxidizable fraction**: Elements bound to active organic matter groups or sulfur compounds that oxidize to soluble sulfate forms.

| Fraction | Extraction method | | | |
|------------------------|---|--|--|--|
| Mild acid-soluble | 0.50g sediment was mixed with 20 mL of 0.11M acetic acid | | | |
| fraction | and centrifuged at a centrifugal force of 3000 g for 20 min. The supernatant was filtered through a 0.45 μ m membrane, transferred to a new centrifuge tube and stored in a refrigerator at 0-4 °C with 1% nitric acid solution for testing. | | | |
| Reducible fraction | Residue from mild acid-soluble fraction was add with 10mL of deionized water, shaken for 15 minutes($22 \degree C \pm 5 \degree C$), and centrifuged (3000g, 20min) to clean residue. The solid residue was extracted with 20mL 0.5 M NH ₂ OH HCl(Dissolve 34.75 g hydroxylamine hydrochloride in 400 ml water, add 25 ml nitric acid (1 + 7), and dilute to the mark. Prepare it freshly before use.), and the extraction steps and measurement steps followed mild acid-soluble fraction. | | | |
| Oxidizable fraction | Steps for cleaning residue was followed reducible fraction. The solid residue was slowly added to 5 mL H ₂ O ₂ in 3 - 4 portions (with nitric acid to adjust pH to 2 - 3). Cover the centrifuge tube and digest at 22 °C± 5 °C for 1 h, shaking it manually every 10 min. Then continue to digest in a constant temperature water bath (85 °C ± 2 °C) for 1 h, also shaking every 10 min. Remove the lid and heat to control the volume to less than 1.5 mL. Take out the centrifuge tube and let it cool. Subsequently, add 5 mL H ₂ O ₂ in 3 - 4 portions again (with nitric acid to adjust pH to 2 - 3), cover it, and digest in the water bath (85 °C ± 2 °C) for 1 h, shaking every 10 min. Remove the lid and neat to control the volume to less than 1.5 mL. Take out the centrifuge tube and let it cool. Subsequently, add 5 mL H ₂ O ₂ in 3 - 4 portions again (with nitric acid to adjust pH to 2 - 3), cover it, and digest in the water bath (85 °C ± 2 °C) for 1 h, shaking every 10 min. Remove the lid and continue heating to control the volume to about 1 mL (avoid drying up). Take out the tube and cool. Finally, add 25 mL of 1 M ammonium acetate solution (NH ₄ Ac, adjusted to pH 2.0 with nitric acid) into the centrifuge tube. The extraction steps and measurement steps followed mild acid-soluble fraction | | | |

Table S5: Extraction methods and procedures for determining metals fractions in Reservoir F sediment

| Characteristic | Mild Acid-Soluble Manganese | Reducible Manganese | Oxidizable Manganese |
|------------------------------|--|--|---|
| Form of Existence | Adsorbed manganese, carbonates, and soluble salts | Manganese oxides (e.g., MnO ₂ , Mn ₂ O ₃) | Organically bound manganese, sulfide-bound manganese |
| Stability | Easily released and highly mobile | Relatively stable, released primarily under anoxic conditions | Stable, but released under oxidative conditions |
| Extraction Conditions | Extracted using weak acids (e.g., acetic acid, HCl) | Extracted with reducing agents (e.g., hydroxylamine hydrochloride) | Extracted using oxidizing agents (e.g., H ₂ O ₂) |
| Environmenta Significance | Indicates short-term release potential and bioavailability | Suggests potential for release under reducing (anoxic) conditions | Indicates potential for release under oxidative conditions |

Table S6: Characteristics and Environmental Significance of Different Forms of Manganese in Sediment

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