Supplementary Material

Soil aggregate breakdown with colloidal particles release and transport in soil: a perspective from column experiments

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(This file contains 3 Texts, 2 Tables, and 7 Figures)

Text S1. The combined determination methods [1-3]

Briefly, the determination procedures are as follows. First, H^+-saturated samples were prepared by washing approximately 100 g soil four times with 500 mL of 0.1 mol L^{-1} HCl, and then with deionized water repeatedly until the solution was free of Cl^- in the suspension. The H^+-saturated soil samples were oven dried at 60 °C and sieved through a 0.25 mm sieve. Second, 10 g H^+-saturated soil sample (triplicates) was transferred to a 150 mL triangular bottle, and an equal volume of 0.0075 mol L^{-1} $Ca(OH)_2$ and NaOH solution was added. After shaking for 24 h, several drops of 1 mol L^{-1} HCl were added to adjust the pH of the suspension to 7. Then, the suspension reached cation exchange reaction equilibrium after another 24 h of shaking and determined the final pH, which was approximately 7. Third, the supernatant was collected after the suspension was centrifuged. The Ca^{2+} and Na^+ concentrations in the supernatant were measured using atomic absorption spectrometry and flame photometer, respectively. Finally, the surface electrochemical properties of soil samples can be calculated by the following Eqs. (S1), (S2), (S3), (S4), (S5):

$$\phi_0 = \frac{2\mathrm{RT}}{(2\beta_{Ca} - \beta_{Na})\mathrm{F}} \ln \frac{a_{Ca}^0 N_{Na}}{a_{Na}^0 N_{Ca}} \tag{S1.}$$

$$\sigma_0 = \mathrm{sgn}(\phi_0)\sqrt{\frac{\varepsilon \mathrm{RT}}{2\pi}\left(a_{Na}^0 \mathrm{e}^{\frac{\beta_{Na}\mathrm{F}\phi_0}{\mathrm{RT}}} + a_{Ca}^0 \mathrm{e}^{\frac{2\beta_{Ca}\mathrm{F}\phi_0}{\mathrm{RT}}}\right)} \tag{S2.}$$

$$E = \frac{4\pi\sigma_0}{\varepsilon} \tag{S3.}$$

$$SSA = \frac{N_{Na}k}{m a_{Na}^0} \mathrm{e}^{\frac{\beta_{Na}\mathrm{F}\phi_0}{2\mathrm{RT}}} \tag{S4.}$$

$$CEC = \frac{10^5 S\sigma}{\mathrm{F}} \tag{S5.}$$

where

$\beta_{Na} = -0.0213\ln(\mathrm{I}^{0.5}) + 1.2331$

$$\beta_{Na} = 2 - \beta_{Ca}$$

$$m = 0.5259\ln\frac{c_{Na}^0 + c_H^0}{c_{Ca}^0} + 1.992$$

$$\kappa = \sqrt{\frac{8\pi F^2 Z^2 c_0}{\varepsilon RT}}$$

where φ_0 (mV) is the surface potential; σ_0 (C m^{-2}) is the surface charge density; E (V m^{-1}) is the surface electric field strength; SSA (m^2 g^{-1}) is the specific surface area; CEC (cmol kg^{-1}) is the cation exchange capacity; R (J K^{-1} mol^{-1}) is the universal gas constant; T (K) is the absolute temperature; F (C mol^{-1}) is the Faraday constant; Z is the charge of each ion species; β_{Na} and β_{Ca} are the corresponding modification factors of Z for Na^+ and Ca^{2+}, respectively; ε is the dielectric constant for water (8.9×10^{-9} C^2 J^{-1} m^{-1}); κ (dm^{-1}) is the Debye-Hückel parameter; I (mol L^{-1}) is the ionic strength; and c^0_{Na} (mol L^{-1}) and c^0_{Ca} (mol L^{-1}) are equilibrium Na^+ and Ca^{2+} concentrations in the bulk solution, respectively.

Text S2. Tracer experiments.

The hydrodynamic conditions of the soil columns were obtain using the tracer experiments [4]. Before tracer experiments, the solution chemistry was stabilized using 20 mM $CaCl_2$ to avoid breakdown of the packed soil aggregate. Then, 20 PVs of 10 mg L^{-1} NO_3^- (KNO_3, because KCl was used in the pre-treatment) were injected to the columns. The effluents were collected every 10 min and analyzed using an ultraviolet-visible spectrophotometer at 201 nm [5].

Text S3. Advection Dispersion Model.

The breakthrough curves of NO_3^- were simulated by the Advection Dispersion Model. The equation was:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} - v\frac{\partial C}{\partial z}$$

where *C* is the concentration of NO_3^- (mg L^{-1}); *D* is the dispersion coefficient (cm^2 min^{-1}); *v* is the Darcy velocity (0.2829 cm min^{-1}); *ρ* is bulk density (g cm^{-3}); *θ* is the porosity. D was calculated using Hydrus-1D software [6].

References:

1. Li, H.; Hou, J.; Liu, X.M.; Li, R.; Zhu, H.L.; Wu, L.S. Combined Determination of Specific Surface Area and Surface Charge Properties of Charged Particles from a Single Experiment. *Soil Sci. Soc. Am. J.* **2011**, *75*, 2128-2135, doi:10.2136/sssaj2010.0301.
2. Liu, J.; Wang, Z.; Hu, F.; Xu, C.; Ma, R.; Zhao, S. Soil organic matter and silt contents determine soil particle surface electrochemical properties across a long-term natural restoration grassland. *CATENA* **2020**, *190*, 104526, doi:10.1016/j.catena.2020.104526.
3. Yu, Z.; Zhang, J.; Zhang, C.; Xin, X.; Li, H. The coupling effects of soil organic matter and particle interaction forces on soil aggregate stability. *Soil Tillage Res.* **2017**, *174*, 251-260, doi:10.1016/j.still.2017.08.004.

Table S1. Fitted parameters of accumulation curves.

KCl Concentration (mol L^{-1})	Fitting equation	R^2
10^{-5}	$y = 29.413\ln(x) - 103.29$	0.992
10^{-3}	$y = 27.805\ln(x) - 96.519$	0.994
10^{-2}	$y = 3.6392\ln(x) - 10.895$	0.981

R^2: correlation coefficient

Table S2. Fitted parameters of accumulation curves.

Distance (nm)	Fitting equation	R^2
1.5 nm	$y = 175.69x - 5467.50$	0.996
2.0 nm	$y = 149.55x - 2434.90$	1.000
4.0 nm	$y = 140.91x - 612.30$	0.999
6.0 nm	$y = 146.22x - 258.33$	0.998
8.0 nm	$y= 155.65x - 128.96$	0.998
9.0 nm	$y = 162.00x - 93.75$	0.997

Figure S1. Map of sampling site.

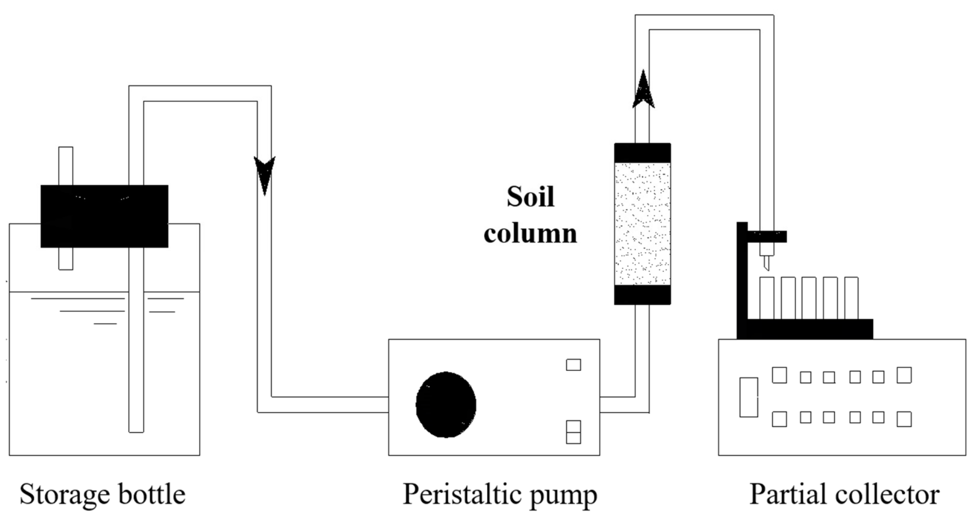

Figure S2. Experimental arrangements.

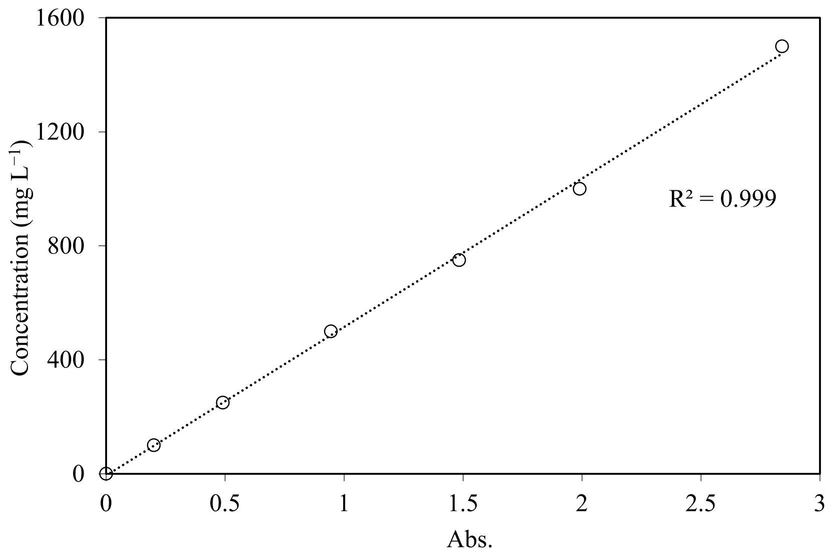

Figure S3. Calibration curve of the Lou soil particles.

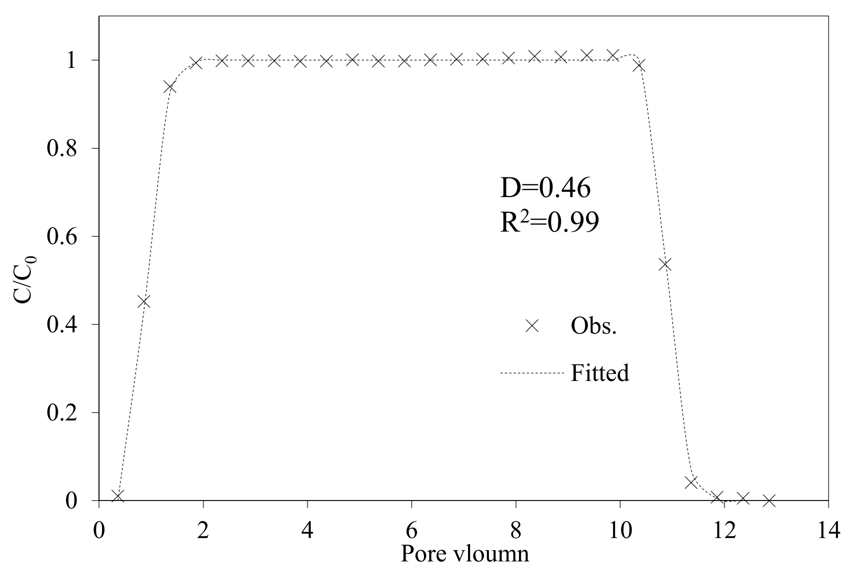

Figure S4. Simulation results of the tracer transport.

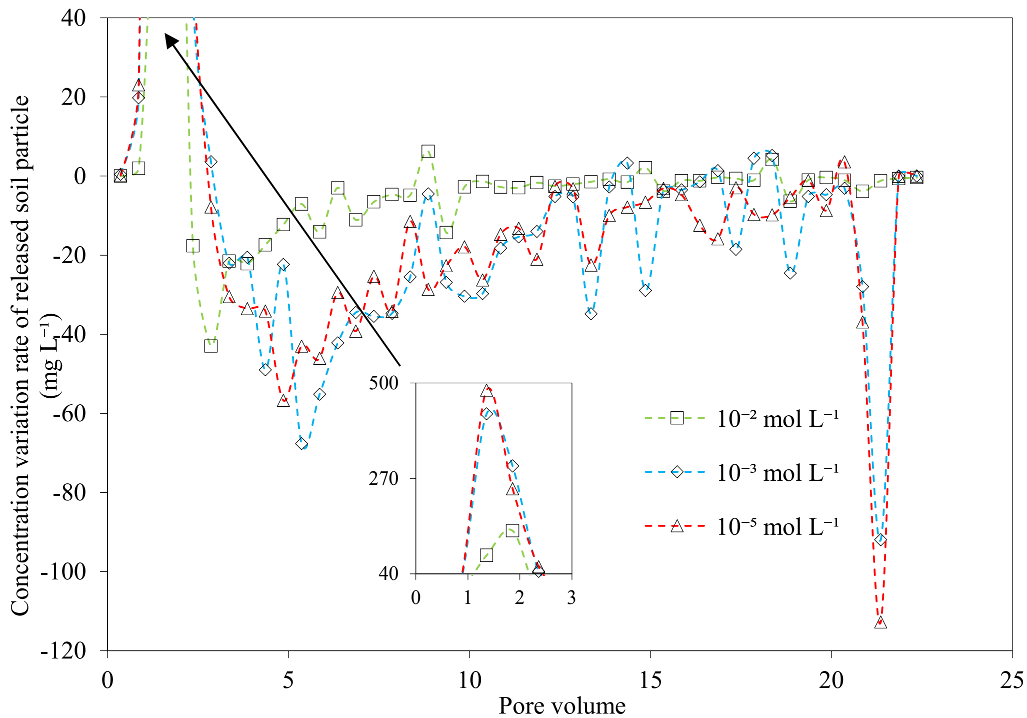

Figure S5. Concentration variation rate of released soil particle.

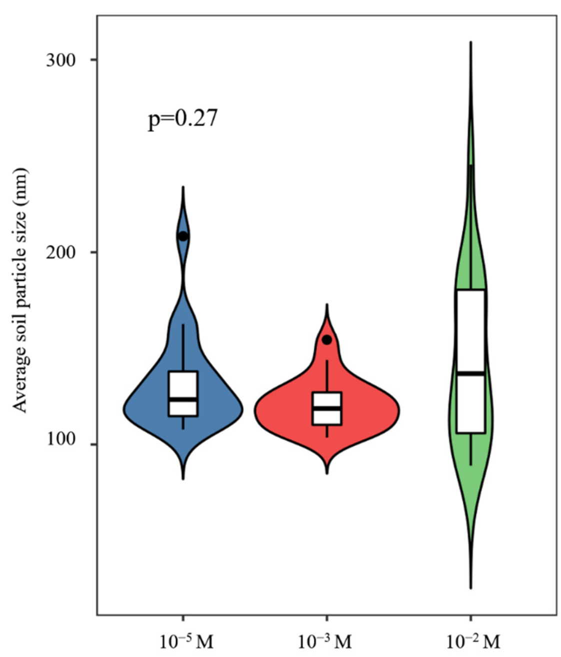

Figure S6. Violin plot of mean particle size of released soil.

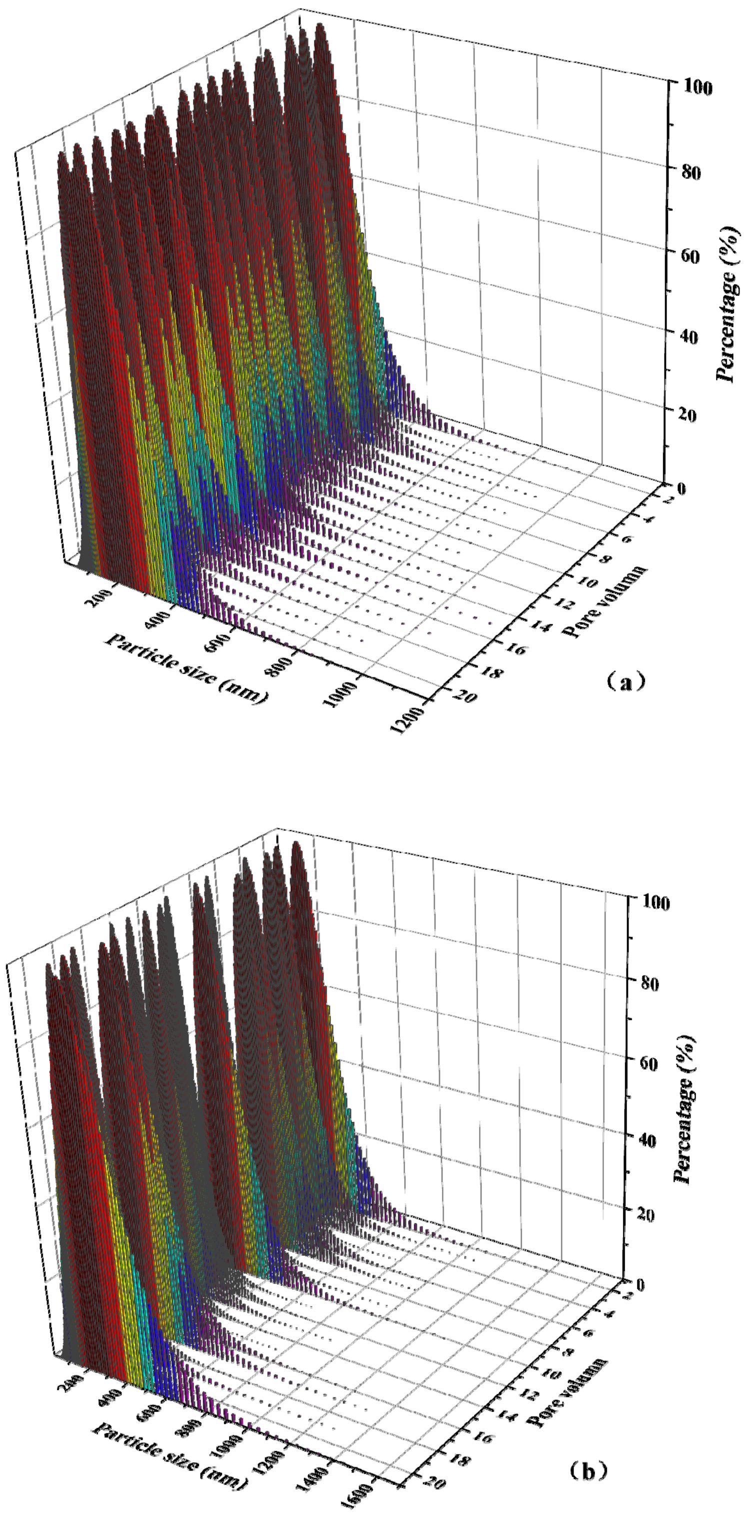

Figure S7. Particle size distribution of soil particle with pore volume under 10^{-5} M (a) and 10^{-2} M (b).