Supplementary Material

Effect of agricultural organic inputs on nanoplastics transport in saturated goethite-coated porous media: Particle size selectivity and role of dissolved organic matter

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**S1. Goethite preparation**

Goethite was prepared with adding 2.5 M NaOH at a speed of 10 ml min$^{-1}$ to 5 L 0.5 M Fe(NO$_3$)$_3$ solution. Keep on mixing the suspension during the addition. And put a pH-electrode in the above suspension to monitor the pH and stop adding NaOH when pH = 12. Then put the suspension in an oven at 60 °C for 4 days to let Fe(OH)$_3$ age. At last, decant the clear solution on the top and dialyze Fe(OH)$_3$ paste until the EC < 10 μS.

**S2. The calibration curves of molecular weights of DOM and humification index calculation**

![Figure S1](image)

Figure S1. The calibration curves of molecular weights of DOM between retention time and standard substances.
According to the soluble organic components detected in the fluorescence spectral distribution, excitation/emission (E\textsubscript{ex}/E\textsubscript{em}) wavelength regions can be considered as humic acid-like areas to demonstrate the humic characteristics of these components \textsuperscript{1}. The humification index (HIX) was calculated as the ratio of the peak integrated area of emission wavelengths ranging from 300 to 345 nm to that of emission wavelengths ranging from 435 to 480 nm, under a 255-nm excitation wavelength \textsuperscript{2}.

S3. The calibration curves of concentrations of nanoplastics and nanoplastics with DOM

Figure S2. The calibration curves of 50NPs (a), 400NPs (b), and NPs-DOM suspension (c-t) concentrations between absorbency and standards at pH 6.0.
### S4. Zeta potential of experimental material

#### Table S1 Zeta potential of NPs and NPs-DOM

| DOM          | Zeta potential (mV) | 50NPs | 400NPs |
|--------------|---------------------|-------|--------|
| -            | -39.8 ± 1.2         | -40.6 ± 0.7 |
| pristine BC<sub>DOM</sub> | -57.2 ± 2.1         | -58.1 ± 1.9 |
| pristine WS<sub>DOM</sub> | -30.4 ± 1.5         | -28.9 ± 1.3 |
| pristine SM<sub>DOM</sub> | -35.0 ± 0.8         | -33.2 ± 1.1 |
| half BC<sub>DOM</sub> | -54.0 ± 0.6         | -55.3 ± 0.5 |
| half WS<sub>DOM</sub> | -32.4 ± 1.8         | -31.7 ± 1.1 |
| half SM<sub>DOM</sub> | -35.9 ± 1.4         | -34.6 ± 0.5 |
| quarter BC<sub>DOM</sub> | -53.6 ± 0.9         | -54.0 ± 0.2 |
| quarter WS<sub>DOM</sub> | -34.3 ± 1.7         | -33.2 ± 0.6 |
| quarter SM<sub>DOM</sub> | -36.6 ± 0.7         | -36.1 ± 1.0 |

#### Table S2 Zeta potential of quartz and GT coated quartz.

| Collector | Quartz | 0.2% GT-Quartz | 0.5% GT-Quartz | 2% GT-Quartz |
|-----------|--------|----------------|----------------|--------------|
| Zeta potential (mV) | -29.2 ± 1.6 | 19.8 ± 0.6 | 26.1 ± 0.9 | 30.2 ± 1.1 |
Table S3 Zeta potential of GT-coated sand (0-2.5, 2.5-5, 5-7.5, and 7.5-10 cm) after co-transport experiment of NPs and DOM.

| Column                               | Zeta potential (mV) |
|--------------------------------------|---------------------|
|                                      | 0-2.5 cm            | 2.5-5 cm         | 5-7.5 cm         | 7.5-10 cm        |
| 2% GT-70μm Quartz pristine BC<sub>DOM</sub> | -16.8 ± 5.1         | -12.4 ± 1.1      | -3.9 ± 2.1       | 8.7 ± 3.1        |
| 2% GT-70μm Quartz pristine WS<sub>DOM</sub> | -10.7 ± 1.4         | 5.0 ± 2.0        | 16.9 ± 2.2       | 24.6 ± 1.6       |
| 2% GT-70μm Quartz pristine SM<sub>DOM</sub> | -27.5 ± 1.8         | -21.2 ± 0.6      | -17.6 ± 2.0      | -15.5 ± 0.5      |
| 2% GT-338μm Quartz pristine BC<sub>DOM</sub> | -15.7 ± 2.6         | -11.1 ± 0.8      | -6.6 ± 1.0       | -3.4 ± 1.3       |
| 2% GT-338μm Quartz pristine WS<sub>DOM</sub> | -6.4 ± 2.8          | 9.2 ± 2.1        | 20.5 ± 0.5       | 25.3 ± 0.1       |
| 2% GT-338μm Quartz pristine SM<sub>DOM</sub> | -24.4 ± 1.3         | -22.2 ± 1.6      | -19.5 ± 1.8      | -18.7 ± 1.0      |
| 0.2% GT-70 μm Quartz pristine BC<sub>DOM</sub> | -28.7 ± 0.6         | -28.2 ± 0.2      | -27.3 ± 1.0      | -22.3 ± 1.4      |
| 0.2% GT-70 μm Quartz pristine WS<sub>DOM</sub> | -26.4 ± 0.9         | -23.6 ± 0.5      | -16.0 ± 1.7      | -14.3 ± 2.2      |
| 0.2% GT-70 μm Quartz pristine SM<sub>DOM</sub> | -29.2 ± 0.1         | -29.0 ± 0.5      | -28.4 ± 0.4      | -27.7 ± 0.8      |
| 0.2% GT-338 μm Quartz pristine BC<sub>DOM</sub> | -29.8 ± 0.1         | -27.2 ± 0.3      | -26.2 ± 0.2      | -24.3 ± 0.6      |
| 0.2% GT-338 μm Quartz pristine WS<sub>DOM</sub> | -25.4 ± 0.4         | -22.0 ± 0.7      | -20.3 ± 0.9      | -15.6 ± 1.2      |
| 0.2% GT-338 μm Quartz pristine SM<sub>DOM</sub> | -29.0 ± 0.5         | -27.0 ± 0.1      | -26.4 ± 1.3      | -25.8 ± 0.7      |
| 2% GT-70μm Quartz half BC<sub>DOM</sub> | 16.2 ± 5.1          | 21.5 ± 2.4       | 23.9 ± 0.9       | 28.7 ± 2.2       |
| 2% GT-70μm Quartz half WS<sub>DOM</sub> | 22.6 ± 0.8          | 25 ± 1.4         | 26.3 ± 3.4       | 28.6 ± 2.5       |
| 2% GT-70μm Quartz half SM<sub>DOM</sub> | -17.4 ± 1.7         | -9.2 ± 4.3       | -7.6 ± 2.7       | -5.5 ± 1.2       |
| 2% GT-338μm Quartz half BC<sub>DOM</sub> | -6.8 ± 3.1          | 5.4 ± 1.3        | 17.5 ± 1.9       | 23.4 ± 2.0       |
| 2% GT-338μm Quartz half WS<sub>DOM</sub> | 15.3 ± 3.6          | 19.7 ± 2.2       | 24.0 ± 1.4       | 27.1 ± 1.8       |
| 2% GT-338μm Quartz half SM<sub>DOM</sub> | -20.2 ± 0.2         | -19.1 ± 0.6      | -18.3 ± 1.3      | -17.9 ± 1.1      |
| 0.2% GT-70 μm Quartz half BC<sub>DOM</sub> | -18.4 ± 1.8         | -14.7 ± 0.4      | -11.6 ± 1.3      | -7.1 ± 2.1       |
| 0.2% GT-70 μm Quartz half WS<sub>DOM</sub> | -14.5 ± 6.2         | -7.7 ± 2.3       | -5.0 ± 3.4       | 4.0 ± 3.4        |
| 0.2% GT-70 μm Quartz half SM<sub>DOM</sub> | -24.4 ± 2.0         | -23.7 ± 1.4      | -22.3 ± 1.0      | -21.0 ± 1.8      |
| 0.2% GT-338 μm Quartz half BC<sub>DOM</sub> | -20.5 ± 0.5         | -19.8 ± 1.1      | -19.2 ± 0.7      | -17.3 ± 0.4      |
| 0.2% GT-338 μm Quartz half WS<sub>DOM</sub> | -21.4 ± 1.2         | -14.6 ± 2.6      | -9.6 ± 1.7       | -5.3 ± 2.9       |
| 0.2% GT-338 μm Quartz half SM<sub>DOM</sub> | -24.7 ± 1.5         | -23.3 ± 0.2      | -21.8 ± 1.8      | -20.8 ± 1.5      |
| 2% GT-70μm Quartz quarter BC<sub>DOM</sub> | -4.2 ± 2.6          | 16.1 ± 2.4       | 27.5 ± 0.5       | 29.4 ± 1.9       |
| 2% GT-70μm Quartz quarter WS<sub>DOM</sub> | 25.6 ± 0.4          | 28.7 ± 0.5       | 30.2 ± 1.1       | 30.3 ± 0.2       |
| 2% GT-70μm Quartz quarter SM<sub>DOM</sub> | -16.6 ± 1.8         | 1.2 ± 5.1        | 22.6 ± 3.2       | 29.8 ± 1.3       |
| 2% GT-338μm Quartz quarter BC<sub>DOM</sub> | 2.7 ± 4.2           | 9.8 ± 4.0        | 28.5 ± 1.3       | 29.6 ± 0.6       |
| 2% GT-338μm Quartz quarter WS<sub>DOM</sub> | 21.5 ± 2.1          | 27.4 ± 2.0       | 28.8 ± 1.6       | 30.2 ± 0.3       |
| 2% GT-338μm Quartz quarter SM<sub>DOM</sub> | -13.9 ± 4.2         | -7.1 ± 3.3       | -2.3 ± 3.8       | 8.5 ± 3.0        |
| 0.2% GT-70 μm Quartz quarter BC<sub>DOM</sub> | -11.4 ± 1.8         | -5.1 ± 2.4       | 4.6 ± 3.3        | 14.1 ± 2.1       |
| 0.2% GT-70 μm Quartz quarter WS<sub>DOM</sub> | -11.5 ± 6.2         | -3.7 ± 2.3       | 7.0 ± 4.4        | 15.5 ± 2.1       |
| 0.2% GT-70 μm Quartz quarter SM<sub>DOM</sub> | -21.2 ± 1.9         | -14.1 ± 2.2      | -5.7 ± 3.8       | 7.0 ± 2.4        |
| 0.2% GT-338 μm Quartz quarter BC<sub>DOM</sub> | -12.3 ± 0.8         | -6.8 ± 1.4       | 3.1 ± 1.7        | 12.5 ± 2.1       |
| 0.2% GT-338 μm Quartz quarter WS<sub>DOM</sub> | -11.7 ± 2.6         | -4.0 ± 3.5       | 9.2 ± 3.2        | 16.7 ± 2.2       |
| 0.2% GT-338 μm Quartz quarter SM<sub>DOM</sub> | -20.2 ± 1.9         | -13.5 ± 2.7      | -7.4 ± 1.7       | 5.9 ± 3.3        |
S5. Nanoparticles transport models

The convection diffusion equation (CDE) with two kinetic retention sites was employed to describe the nanoparticle transport and retention in the column experiments as equation (1)\(^3\).\(^4\).

\[
\frac{\partial C}{\partial t} = -v \frac{\partial C}{\partial x} + D \frac{\partial^2 C}{\partial x^2} - \rho \frac{\partial S_1}{\partial t} - \rho \frac{\partial S_2}{\partial t}
\]

\(\theta\) (cm\(^3\)·cm\(^{-3}\)) is the volumetric water content; \(D\) is the dispersion coefficient (m\(^2\)·s\(^{-1}\)); \(\rho\) (g·m\(^{-3}\)) is the column dry bulk density; \(x\) (cm) is the spatial coordinate; \(v\) (cm·min\(^{-1}\)) is the Darcy’s velocity; and \(S_1\) (g·g\(^{-1}\)) and \(S_2\) (g·g\(^{-1}\)) are nanoparticle concentrations deposited in Site1 and Site2, respectively.

The Site1, first kinetic site, on which the retention of the nanoparticle is assumed to be reversible, whereas Site2, the second kinetic site, on which the retention is assumed to be irreversible, as described by the depth-dependent retention. \(S_1\) on Site1 and \(S_2\) on Site2 are given in equations (2) and (3), respectively.

\[
\rho \frac{\partial S_1}{\partial t} = k_{1a} C - \frac{\rho}{\theta} k_{1d} S_1
\]

\[
\rho \frac{\partial S_2}{\partial t} = \psi_t k_{2a} C
\]

\(k_{1a}\) (min\(^{-1}\)) and \(k_{2a}\) (min\(^{-1}\)) are first-order retention coefficients on Site1 and Site2, respectively; \(k_{1d}\) (min\(^{-1}\)) is the first-order detachment coefficient; \(\psi_t\) (dimensionless) is the nanoparticle attachment function to account for the depth-dependent behavior of particle attachment expressed by equations (4):

\[
\psi_t = \left(\frac{d_c + x - x_0}{d_c}\right)^{-\beta}
\]

\(d_c\) is the median diameter of the sand grains (cm); \(x_0\) is the coordinate of the location where the straining process starts; and \(\beta\) (dimensionless) is an empirical
variable that controls the shape of the retention profile, using an optimal value of 0.432 for different sized spherical nanoparticle and sand grains in which significant depth-dependency (hyperexponential retention profiles) occurred \(^4\). Three parameters, including \(k_{1a}\), \(k_{2a}\), and \(k_{1d}\), were fitted.

**S6. DLVO theory**

The representative Derjaguin-Landau-Verwey-Overbeek (DLVO) theory was used to qualitatively understand the NPs transport and retention in water-saturated sands columns through calculating the total particle-sand interaction energy as the sum of Lifshitz-van der Waals (LW) and electrical double layer (EDL) interactions \(^5,6\). Ionic strength stays constant at 0.1 mM NaCl. The equation of the LW interaction energy \((E_{\text{LW}})\) is given as follows \(^7,8\):

\[
E_{\text{LW}} = -\frac{A_{132}d_p}{12h} \left[1 + \frac{14h}{\lambda}\right]^{-1} \quad (5)
\]

\(d_p\) is the diameter of nanoparticle; \(h\) is the separation distance between the nanoparticle and sand surface; \(\lambda\) is the characteristic wavelength of interaction and was defined as 100 nm; \(A_{132}\) is the Hamaker constant of particle-water-sand, which can be expressed by equation (6):

\[
A_{132} = (\sqrt{A_{11}} - \sqrt{A_{33}})(\sqrt{A_{22}} - \sqrt{A_{33}}) \quad (6)
\]

\(A_{11}\) is the Hamaker constant for NPs \(6.60 \times 10^{-20}\text{ J}\) \(^9\); \(A_{22}\) is the Hamaker constant for quartz sand \(8.86 \times 10^{-20}\text{ J}\) \(^10\); \(A_{33}\) is the Hamaker constant for water \(3.7 \times 10^{-20}\text{ J}\) \(^9\).

The equation of EDL interaction energy \((E_{\text{EDL}})\) is given as follows \(^11,12\):
\[ E_{\text{EDL}} = 0.5 \pi \varepsilon_0 \varepsilon_r d_p \left\{ 2 \psi_p \psi_c \ln \left[ \frac{1 + \exp \left( -\kappa h \right)}{1 - \exp \left( -\kappa h \right)} \right] + (\psi_p^2 + \psi_c^2) \ln \left[ 1 - \exp \left( -2\kappa h \right) \right] \right\} \] (7)

\[ \varepsilon_0 \text{ is the dielectric permittivity of vacuum (8.854×10}^{-12}\text{ F·m}^{-1}); \varepsilon_r \text{ is the relative dielectric permittivity of water (78.5); } \psi_p \text{ and } \psi_c \text{ are the zeta potentials of NPs and GT-coated sand, respectively; } \kappa (\text{m}^{-1}) \text{ is the Debye-Hüchel parameter, which is expressed by equation (8);} \]

\[ \kappa = 3.28 \times 10^9 (I)^{1/2} \] (8)

\[ I \text{ is ionic strength.} \]
S7. Typical DOM selection reason and their molecular formula

A part of the polysaccharides in WS<sub>DOM</sub> and SM<sub>DOM</sub> may be directly or indirectly derived from the cellulose (CL) in plant cell walls; thus, CL was selected to represent polysaccharides. Amylose (AM) was also selected as a common polysaccharide. Both plant and animal lipids mostly comprise long chains with an ester carbonyl group; thus, oleic acid (OA) represented lipid-like compounds. Moreover, a tetrapeptide (TP, valine-glycine-serine-alanine) was chosen to represent proteins. Furthermore, HA and fulvic acid (FA) were considered as typical DOM. Two hundred original configurations were generated, and each configuration was then optimized based on Parameterized Model number 6. The first thirty configurations with the lowest energies were further optimized based on the all-electron density functional theory (DFT) at B3LYP/3-21G(d) level using Gaussian 16<sup>13</sup>. The optimized configuration with the lowest energy was then further optimized at B3LYP/6-31G(d) level. Finally, the single-point energy was calculated at the B3LYP/6-311G(d) level. Grimme’s D3BJ dispersion was used to describe the inter-molecular interactions.
Figure S3. Molecular formula of typical DOM, molecular structure of HA and FA cited from Ouni, et al.\textsuperscript{14}. The blue-green, white, red, and blue spheres represent C, O, H, and N, respectively.

S8. Calculation of binding energy

The equation of binding energy between different species NPs and DOM is given as follows:

$$\text{Binding energy} = E_{\text{complex}} - (E_{\text{fragment1}} + E_{\text{fragment2}}) \quad (9)$$

Where $E_{\text{complex}}$ represents the energy of a complex composed of two molecules, and $E_{\text{Fragment1}}$ and $E_{\text{Fragment2}}$ represent the energy of a single molecule corresponding to different systems.
### S9. Fitted parameters of nanoplastics transport in the GT coated sand columns

Table S4. Fitted parameters of NPs transport in different ratio GT coated 70 µm and 338 µm sand columns at pH 6.0.

| NPs       | Column          | \(k_{1a}\) \(\text{a} \) (min\(^{-1}\)) | \(k_{3d}\) \(\text{b} \) (min\(^{-1}\)) | \(k_{2a}\) \(\text{c} \) (min\(^{-1}\)) | \(k_{1d}/k_{1a}\) | \(R^2\) \(\text{d} \) | Recovery \(\text{e} \) (%) |
|-----------|-----------------|---------------------------------|---------------------------------|---------------------------------|-----------------|--------------------|--------------------------|
| 70 µm Quartz | 0.2% GT-70 µm Quartz | 1.22 ± 0.35                      | 0.008 ± 0.002                   | 0.000 ± 0.000                   | 0.006±0.000    | 0.988 ± 0.001     | 88.0 ± 1.3       |
| 70 µm Quartz | 0.5% GT-70 µm Quartz | 1.59 ± 0.13                      | 0.001 ± 0.000                   | 0.013 ± 0.007                   | 0.000±0.000    | 0.998 ± 0.001     | 75.8 ± 2.5        |
| 70 µm Quartz | 2% GT-70 µm Quartz | 1.16 ± 0.02                      | 0.000 ± 0.000                   | 0.000 ± 0.000                   | 0.000±0.000    | 0.996 ± 0.001     | 59.1 ± 2.3        |
| 338 µm Quartz | 0.2% GT-338 µm Quartz | 0.45 ± 0.19                      | 0.003 ± 0.001                   | 0.000 ± 0.000                   | 0.007±0.000    | 0.99 6± 0.003     | 92.9 ± 2.2        |
| 338 µm Quartz | 0.5% GT-338 µm Quartz | 0.34 ± 0.07                      | 0.024 ± 0.001                   | 0.000 ± 0.000                   | 0.074±0.012    | 0.969 ± 0.002     | 94.5 ± 2.7        |
| 338 µm Quartz | 2% GT-338 µm Quartz | 0.38 ± 0.03                      | 0.003 ± 0.002                   | 0.014±0.004                     | 0.008±0.005    | 0.985 ± 0.006     | 86.9 ± 1.4        |
| 70 µm Quartz | 50NPs 0.2% GT-70 µm Quartz | 2.17 ± 2.07                      | 4.33 ± 4.11                     | 0.114 ± 0.005                   | 2.07±0.08      | 0.993 ± 0.006     | 91.9 ± 1.4        |
| 70 µm Quartz | 50NPs 0.5% GT-70 µm Quartz | -                               | -                               | -                               | -              | -                  | -            |
| 70 µm Quartz | 50NPs 2% GT-70 µm Quartz | -                               | -                               | -                               | -              | -                  | 0.1 ± 0.0       |
| 338 µm Quartz | 50NPs 0.2% GT-338 µm Quartz | 3.41 ± 0.20                      | 7.93 ± 0.46                     | 0.031 ± 0.003                   | 2.32±0.000     | 0.999 ± 0.000     | 94.9 ± 0.5        |
| 338 µm Quartz | 50NPs 0.5% GT-338 µm Quartz | 0.62 ± 0.18                      | 0.000 ± 0.000                   | 1.112 ± 0.581                   | 0.000±0.000    | 0.963 ± 0.022     | 6.3 ± 1.2        |
| 338 µm Quartz | 50NPs 2% GT-338 µm Quartz | -                               | -                               | -                               | -              | -                  | -            |

\(a\) The first-order retention coefficient on Site1.

\(b\) The first-order detachment coefficient on Site1.

\(c\) The first-order retention coefficient on Site2.

\(d\) Squared Pearson’s correlation coefficient.

\(e\) Recovery of NPs in the effluent.
S10. DLVO interaction energy between nanoplastics and (GT-coated) sand

Figure S4. DLVO interaction energy ($E_{\text{TOT}}$) between NPs and (GT-coated) sand. The $E_{\text{TOT}}$ is expressed in kT, where k is the Boltzmann constant and T is the absolute temperature in Kelvin.

S11. The contents of starch, hemicellulose, cellulose, and lignin in the agricultural organic inputs

The contents of starch, hemicellulose, cellulose, and lignin in BC, SW, and SM were determined using an enzymatic method $^{15,16}$.  

Table S5. The contents of starch, hemicellulose, cellulose, and lignin in the BC, SW, and SM

| Agricultural organic inputs | starch (%) | hemicellulose (%) | cellulose (%) | lignin (%) |
|-----------------------------|------------|-------------------|---------------|------------|
| BC                          | 0.000 ± 0.000 | 0.00 ± 0.00      | 0.75 ± 0.08   | 2.75 ± 0.08 |
| WS                          | 0.071 ± 0.014 | 28.14 ± 0.19     | 38.72 ± 0.14  | 7.17 ± 0.20 |
| SM                          | 0.057 ± 0.009 | 9.54 ± 0.44      | 10.05 ± 0.16  | 7.39 ± 0.36 |
S12. FTIR characteristics of nanoplastics and FTIR differential spectra analysis

The series absorption peaks at 3085, 3062, and 3025 cm\(^{-1}\) were attributed to the C-H stretching vibration of the benzene ring, and the series absorption peaks at 2924 and 2852 cm\(^{-1}\) were assigned to the C-H stretching vibration of methylene. The stair-stepping peaks at 1604 cm\(^{-1}\), 1494 cm\(^{-1}\), and 1451 cm\(^{-1}\) were related to the C=C stretching vibration of the benzene ring, and the absorption peaks at 756 cm\(^{-1}\) and 700 cm\(^{-1}\) were assigned to the C-H bending vibration of the benzene ring.

Figure S5. FTIR differential spectra analysis between different 50NPs-DOM and 50NPs
S13. Transport of different DOM

For individual DOM transport, particularly in 2% GT-coated 70-μm sand, the high content of GT and fine sand might cause DOM retention in the column (Fig. S6). Negatively charged DOM was readily adsorbed on GT during transport, forming a ligand exchange between the carboxyl/hydroxyl functional groups of DOM and the GT surface\textsuperscript{17}. The retention of DOM significantly changed the properties of the GT-coated sand. The retention rate was the highest (average: 43.0\%) in BC\textsubscript{DOM} because of its low concentration (Table S6); however, the amount retained in the column was low. The retention rate of WS\textsubscript{DOM} (average: 36.2\%) was higher than that of SM\textsubscript{DOM} (average: 20.9\%) (Table S6). WS\textsubscript{DOM} was readily deposited in the 2% GT-coated 70-μm sand column (71\%) (Fig. S6 and Table S6) because the protein-like substance in DOM promoted the formation of bridged complexes with GT and organic molecules\textsuperscript{18}, and the small pore structure facilitated this process.
Figure S6. Breakthrough curves (a, c, and e) and RPs (b, d, and f) of BC$_{DOM}$ (a and b), WS$_{DOM}$ (c and d), and SM$_{DOM}$ (e and f) at pH 7.0. The DOM RPs were plotted as the initial DOM concentration normalized (DOM retention in the sands columns S, divided by initial DOM concentration) as DOM retention per gram of dry sand as a function of distance from the column inlet. Symbols and solid lines show the observed data and simulation fitting, respectively.
S14. Fitted parameters of DOM transport in the GT coated sand columns

Table S6. Fitted parameters of transport of DOM released from BC, WS, and SM in the 0.2% and 2% GT coated 70 μm and 338 μm sand columns at pH 6.0.

| DOM  | Column            | $k_{1d}$ (min$^{-1}$) | $k_{1d}$ (min$^{-1}$) | $k_{2a}$ (min$^{-1}$) | $k_{1d}/k_{1a}$ R$^2$ | Recovery (%) |
|------|-------------------|-----------------------|-----------------------|-----------------------|------------------------|--------------|
|      |                   | Effluent              | Column                | Total                 |
| BC$^{\text{DOM}}$ | 0.2% GT-70 μm Quartz | 0.125 | 0.016 | 0.005 | 0.127 | 0.931 | 67.52 | 35.25 | 102.77 |
|      | 2% GT-70 μm Quartz | 0.143 | 0.012 | 0.549 | 0.082 | 0.825 | 40.50 | 61.98 | 102.48 |
|      | 0.2% GT-338 μm Quartz | 0.084 | 0.022 | 0.027 | 0.262 | 0.951 | 80.22 | 21.32 | 101.54 |
|      | 2% GT-338 μm Quartz | 0.129 | 0.028 | 0.399 | 0.217 | 0.811 | 45.92 | 53.40 | 99.32  |
| WS$^{\text{DOM}}$ | 0.2% GT-70 μm Quartz | 0.537 | 0.225 | 0.273 | 0.418 | 0.995 | 83.17 | 18.30 | 101.47 |
|      | 2% GT-70 μm Quartz | 0.304 | 0.186 | 2.061 | 0.612 | 0.954 | 26.25 | 70.14 | 96.39  |
|      | 0.2% GT-338 μm Quartz | 0.603 | 0.019 | 0.112 | 0.032 | 0.975 | 81.6  | 16.79 | 98.39  |
|      | 2% GT-338 μm Quartz | 0.373 | 0.045 | 0.446 | 0.119 | 0.990 | 50.81 | 39.72 | 90.53  |
| SM$^{\text{DOM}}$ | 0.2% GT-70 μm Quartz | 0.300 | 0.200 | 0.100 | 0.666 | 0.994 | 94.03 | 7.78  | 101.81 |
|      | 2% GT-70 μm Quartz | 0.250 | 0.061 | 0.900 | 0.244 | 0.979 | 53.32 | 44.16 | 97.48  |
|      | 0.2% GT-338 μm Quartz | 0.589 | 0.206 | 0.026 | 0.350 | 0.994 | 94.81 | 6.96  | 101.77 |
|      | 2% GT-338 μm Quartz | 0.785 | 0.568 | 0.251 | 0.724 | 0.964 | 71.74 | 24.79 | 96.53  |
**S15. Fitted parameters of nanoplastics co-transport with DOM in the GT coated sand columns**

Table S7. Fitted parameters of NPs co-transport with different concentrations DOM released from BC, WS, and SM in the 0.2% and 2% GT coated 70 μm and 338 μm sand columns at pH 6.0.

| NPs     | Column                  | DOM      | $k_{1a}$ (min$^{-1}$) | $k_{1d}$ (min$^{-1}$) | $k_{2a}$ (min$^{-1}$) | $k_{1d}/k_{1a}$ | $R^2$             | Recovery (%)     |
|---------|-------------------------|----------|-----------------------|-----------------------|-----------------------|-----------------|-------------------|-----------------|
| 50NPs   | quarter BC$_{DOM}$      | -        | -                     | -                     | -                     | -               | -                 | 0.0 ± 0.0       |
| 2% GT-70 μm Quartz | quarter WS$_{DOM}$  | 0.67 ± 0.24 | 0.308 ± 0.308 | 1.957 ± 1.956 | 0.342 ± 0.340 | 0.823 ± 0.118 | 8.3 ± 0.1      |
|         | quarter SM$_{DOM}$      | -        | -                     | -                     | -                     | -               | -                 | 4.0 ± 0.2       |
| 2% GT-338 μm Quartz | quarter BC$_{DOM}$  | 0.25 ± 0.04 | 0.001 ± 0.001 | 0.025 ± 0.023 | 0.005±0.004 | 0.989±0.008 | 71.5 ± 2.7     |
|         | quarter WS$_{DOM}$      | 0.18 ± 0.01 | 0.004 ± 0.002 | 0.086 ± 0.006 | 0.023±0.011 | 0.982±0.01   | 74.6 ± 0.5     |
|         | quarter SM$_{DOM}$      | 0.24 ± 0.01 | 0.002 ± 0.001 | 0.169 ± 0.018 | 0.009±0.004 | 0.983±0.008 | 54.5 ± 1.3     |
| 0.2% GT-70 μm Quartz | quarter BC$_{DOM}$  | -        | -                     | -                     | -                     | -               | -                 | 0.0 ± 0.0       |
|         | quarter WS$_{DOM}$      | -        | -                     | -                     | -                     | -               | -                 | 0.8 ± 0.1       |
|         | quarter SM$_{DOM}$      | -        | -                     | -                     | -                     | -               | -                 | 4.0 ± 0.4       |
| 400NPs  | quarter BC$_{DOM}$      | 0.35 ± 0.02 | 0.002±0.001 | 1.228±0.120 | 0.005±0.004 | 0.930±0.016 | 10.3±0.5        |
| 0.2% GT-338 μm Quartz | quarter WS$_{DOM}$  | 0.29 ± 0.02 | 0.007±0.003 | 1.198±0.065 | 0.024±0.001 | 0.946±0.001 | 14.0±0.9        |
|         | quarter SM$_{DOM}$      | 0.56 ± 0.03 | 0.000±0.000 | 0.934±0.143 | 0.000±0.000 | 0.892±0.026 | 14.6±2.4        |
| 50NPs   | half BC$_{DOM}$         | 1.04 ± 0.72 | 0.409±0.174 | 2.900±0.034 | 0.532±0.200 | 0.932±0.002 | 15.6±0.1        |
| 2% GT-70 μm Quartz | half WS$_{DOM}$       | 1.41 ± 1.00 | 0.980±0.980 | 1.542±1.539 | 0.406±0.406 | 0.858±0.074 | 12.5±1.4        |
|         | half SM$_{DOM}$         | -        | -                     | -                     | -                     | -               | -                 | 3.4 ± 2.4       |
| 2% GT-338 μm Quartz | half BC<sub>DOM</sub> | 0.37 ± 0.05 0.001 ± 0.000 0.073 ± 0.035 0.002 ± 0.000 0.991 ± 0.003 58.5 ± 2.6 |
|----------------------|----------------------|----------------------------------------------------------|
|                      | half WS<sub>DOM</sub>| 0.22 ± 0.01 0.002 ± 0.000 0.144 ± 0.025 0.011 ± 0.000 0.987 ± 0.002 59.3 ± 0.2 |
|                      | half SM<sub>DOM</sub>| 0.34 ± 0.00 0.002 ± 0.000 0.264 ± 0.061 0.006 ± 0.000 0.981 ± 0.003 41.4 ± 1.9 |
| 0.2% GT-70 μm Quartz | half BC<sub>DOM</sub> | 1.57 ± 0.64 0.010 ± 0.005 0.394 ± 0.394 0.006 ± 0.001 0.942 ± 0.020 24.3 ± 1.6 |
|                      | half WS<sub>DOM</sub>| 0.45 ± 0.01 0.009 ± 0.009 2.733 ± 0.346 0.019 ± 0.019 0.907 ± 0.017 7.5 ± 1.2 |
|                      | half SM<sub>DOM</sub>| 0.481 ± 0.027 0.027 ± 0.004 0.277 ± 0.001 0.057 ± 0.012 0.982 ± 0.002 72.5 ± 1.3 |
| 400NPs               | pristine BC<sub>DOM</sub> | 0.480 ± 0.150 0.178 ± 0.143 2.910 ± 0.807 0.308 ± 0.203 0.682 ± 0.125 12.3 ± 2.2 |
|                      | pristine WS<sub>DOM</sub>| 0.208 ± 0.085 0.158 ± 0.056 2.655 ± 0.005 0.780 ± 0.049 0.955 ± 0.006 18.5 ± 0.1 |
|                      | pristine SM<sub>DOM</sub> | - - - - - - |
| 50NPs                | pristine BC<sub>DOM</sub> | 0.517 ± 0.050 0.000 ± 0.000 0.264 ± 0.019 0.000 ± 0.000 0.924 ± 0.023 47.0 ± 0.4 |
|                      | pristine WS<sub>DOM</sub>| 0.249 ± 0.001 0.000 ± 0.000 0.372 ± 0.008 0.000 ± 0.000 0.928 ± 0.003 46.7 ± 1.3 |
|                      | pristine SM<sub>DOM</sub> | 0.369 ± 0.001 0.006 ± 0.001 0.315 ± 0.184 0.015 ± 0.001 0.955 ± 0.015 38.4 ± 3.0 |
| 400NPs               | pristine BC<sub>DOM</sub> | 1.362 ± 0.072 0.064 ± 0.020 0.186 ± 0.028 0.048 ± 0.017 0.969 ± 0.007 71.7 ± 3.9 |
|                      | pristine WS<sub>DOM</sub>| 2.543 ± 0.178 0.010 ± 0.001 0.386 ± 0.037 0.004 ± 0.001 0.901 ± 0.019 29.0 ± 1.4 |
|                      | pristine SM<sub>DOM</sub> | 0.764 ± 0.059 0.052 ± 0.020 0.262 ± 0.004 0.070 ± 0.032 0.983 ± 0.002 76.7 ± 1.6 |
| 0.2% GT-338 μm Quartz | pristine BC<sub>DOM</sub> | 0.363 ± 0.012 0.024 ± 0.004 0.000 ± 0.000 0.065 ± 0.009 0.965 ± 0.009 84.8 ± 0.2 |
|                      | pristine WS<sub>DOM</sub>| 0.331 ± 0.007 0.016 ± 0.003 0.002 ± 0.002 0.049 ± 0.008 0.976 ± 0.003 78.8 ± 0.1 |
|                      | pristine SM<sub>DOM</sub> | 0.802 ± 0.327 0.430 ± 0.420 0.043 ± 0.019 0.388 ± 0.365 0.981 ± 0.009 88.2 ± 0.0 |
S16. Stability of DOM and its influence on the stability of nanoplastics

Settling experiments of individual NPs and pristine DOM and NPs-DOM (with different DOM concentrations) at pH 6.0 were studied. In settling experiments, the influent concentrations of the 50NPs and 400MPs were maintained at 100 mg L\(^{-1}\). Each suspension was immediately transferred into cuvettes for the measurement of absorbance at 300 nm over a period of 24 h. All settling experiments were conducted in duplicate. The settling curves were then plotted, whereby the ordinate was the ratio of the absorbance values at a given point in time \((A)\) to the initial absorbance \((A_0)\) and the abscissa was time.

![Figure S7. The settling curve of different DOM.](image.png)
Figure S8. The settling curve of NPs with and without different DOM.
S17. DLVO interaction energy between nanoplastics and GT-coated sand before and after co-transport with DOM

Figure S9. DLVO interaction energy between NPs and sand before (red lines) and after (others) co-transport experiments of NPs and pristine DOM. The $E_{TOT}$ after co-transport experiment were calculated based on four segmented columns (0-2.5, 2.5-5, 5-7.5, and 7.5-10 cm).

S18. Deposition of nanoplastics

Figure S10. SEM images of NPs deposited on GT coated sand.
S19. XPS results of nanoplastics and different DOM co-deposited on GT coated sand

Figure S11. X-ray photoelectron spectroscopy of 50NPs co-transport with different DOM deposited on GT-coated sand. Data was identified by X-ray photoelectron spectroscopy with an Al Kα X-ray source (1486.6 eV). Survey spectra were recorded from 1200 ~ 0 eV for each sample in a vacuum of 8 × 10^{-10} Pa. All peaks were calibrated using the C1s peak at 284.8 eV. The data was processed using the XPSPEAK 4.1.
### Table S8 Area vertex coordinates and mutual penetration distance.

| System   | Position | Vertex Coordinate 1 | Vertex Coordinate 2 | Mutual penetration distance (Å) |
|----------|----------|---------------------|---------------------|--------------------------------|
|          |          | x       | y       | z       | x       | y       | z       |                        |
| NPs-CL   | A        | 5.72    | -0.42   | -3.51   | 6.18    | -1.18   | -2.94   | 1.050                   |
|          | B        | -3.69   | -0.13   | -0.78   | -3.41   | -1.06   | -0.03   | 1.226                   |
|          | C        | -5.17   | -1.35   | -2.23   | -4.92   | -2.27   | -1.64   | 1.128                   |
| NPs-AM   | A        | 5.40    | -2.81   | 2.38    | 5.40    | -2.18   | 2.36    | 0.635                   |
|          | B        | 1.68    | -0.75   | 3.98    | 1.72    | 0.06    | 4.17    | 0.831                   |
|          | C        | -4.34   | -4.01   | 3.75    | -3.31   | -3.62   | 4.34    | 1.249                   |
| NPs-OA   | A        | 3.13    | 0.99    | -3.50   | 2.92    | 0.79    | -3.70   | 0.359                   |
|          | B        | 1.94    | 1.26    | -1.58   | 1.83    | 1.23    | -1.74   | 0.201                   |
|          | C        | 0.92    | 1.83    | -2.93   | 0.94    | 1.68    | -3.01   | 0.168                   |
| NPs-TP   | A        | 2.67    | 1.10    | -3.29   | 1.75    | 1.43    | -2.76   | 1.119                   |
|          | B        | 0.15    | -2.63   | -4.23   | 0.07    | -2.39   | -4.23   | 0.252                   |
|          | C        | -3.92   | -2.25   | -3.92   | -3.49   | -2.45   | -3.02   | 1.010                   |
| NPs-HA   | A        | 6.026   | 3.116   | 0.908   | 5.947   | 3.355   | -0.123  | 1.061                   |
|          | B        | 4.069   | 3.773   | 3.078   | 4.61    | 2.943   | 3.586   | 1.113                   |
|          | C        | 1.397   | 3.62    | 3.329   | 1.109   | 2.664   | 3.119   | 1.020                   |
| NPs-FA   | A        | -4.418  | 3.576   | -2.299  | -5.249  | 3.718   | -2.993  | 1.092                   |
|          | B        | -1.521  | -2.085  | -3.685  | -2.034  | -3.068  | -4.184  | 1.216                   |
|          | C        | -0.843  | -3.903  | -3.590  | -1.356  | -4.375  | -3.983  | 0.800                   |

### Table S9 Binding energy between representative DOM and NPs.

| System   | Binding energy (kJ mol⁻¹) | Binding energy (Hartree) | E_{complex} (Hartree) | E_{fragment1} (Hartree) | E_{fragment2} (Hartree) |
|----------|--------------------------|--------------------------|-----------------------|-------------------------|-------------------------|
| NPs-CL   | -178.29                  | -0.0679                  | -3685.317             | -1240.301               | -2444.948               |
| NPs-AM   | -158.609                 | -0.0604                  | -3748.058             | -1240.290               | -2507.707               |
| NPs-OA   | -117.76                  | -0.0449                  | -2096.255             | -1240.302               | -855.908                |
| NPs-TP   | -121.81                  | -0.0464                  | -2420.979             | -1240.299               | -1180.634               |
| NPs-HA   | -169.92                  | -0.0647                  | -7059.133             | -1240.305               | -5818.764               |
| NPs-FA   | -166.08                  | -0.0633                  | -3639.782             | -1240.302               | -2399.417               |

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