

Supplementary Material

Chemicals and reagents

Sulfamethoxazole (SMX), Trimethoprim (TMP) were from Dr Ehrenstorfer (Augsburg, Germany), with purity > 99%. The physicochemical properties of SMX and TMP are listed in Table 1. UPLC/MS/MS methanol and acetonitrile were from Merck (Darmstadt, Germany). Formic acid (FA), sodium azide (NaN_3) was purchased from Fisher Scientific (Pittsburgh, PA, USA). Milli-Q water (18.2 M Ω) was produced from a Millipore purification system (Millipore, USA). Individual stock solutions of sulfonamide antibiotics were prepared by dissolving 0.05 mg of two compounds in 50 mL of methanol in amber bottles and stored in dark at -20 °C. Working solutions of 1 mg·L⁻¹ and 20 µg·L⁻¹ were prepared by dilution of stock solutions of with Milli-Q water prior to each experimental run. Deionized water was produced from Aquapro (AR2-100L-P00, containing some ions with low concentration as a result of long-time using). Ion Chromatography Instrument is made of Dionex (Sunnyvale, USA). The model number of anion chromatography and positive ion chromatography is respectively dionex ICS1000 and dionex ICS2000. Inductively coupled plasma mass spectrometry (ICP-MS) is from ThermoFisher, Germany and the model number is X Series 2. 1 g·L⁻¹ standard solutions of K⁺, Na⁺, Ca²⁺, Mg²⁺ are from national central of analysis and testing for nonferrous metals and electronic materials.

Preparation of artificial composite soil column (ASC) studies

The outlet of each ASC was connected to a capped 200 mL amber bottles. 20 L deionized water blended with SMX and TMP was quickly stirred as influent. The influent put in 20 L brown bottles was pumped through these columns at a constant flow rate (5 mL·min⁻¹). After ASCs were set up, use 0.01 mol·L⁻¹ CaCl₂ deionized solution to clean ASCs for 14 d and conduct the removal experiments for 60 d. After 60 d experiment, use deionized water to backwash ASCs for 10 d and the influent was changed to deionized water for 7 d. Before ASCs was packed, the coarse medium sands was sieved and the homogenized fraction > 1 mm was used. Volcanics, clay ceramsites, silty clay and coarse medium sands were filled in these ASCs. These ASCs were designed four parts, that is, the supporting layer (15 cm), the lower layer (25 cm), the upper layer (15 cm) and overflow layer (10 cm) from the bottom up. In the supporting layer, 2 - 5 cm graded cobblestones were filled and a filter screen for preventing clay ceramsites leaking down was added on the upper of the supporting. Then the lower layer was made of clay ceramsites. Also, there is a filter screen on the upper of the lower layer.

After cleaning these ASCs with 0.01 mol·L⁻¹ CaCl₂ solution for 14 d, infiltration rate of each ASC was measured. After preparing 17 - 32 µg·L⁻¹ TMP and SMX solution, solutions were pumped with the flow rate of 5 mL·min⁻¹ and hydraulic loading was 1.13 m·d⁻¹ in columns 1 - 4. The infiltration rate and average porosity of four columns were in Table 3. Because the infiltration rate was low in

column 4, column 4 will overflow with the flow rate of $5 \text{ mL} \cdot \text{min}^{-1}$. In this study, column 4 kept a 2 centimeter water level and excess water was discharged from overflow pipe. These ASCs had worked for one day and had been stopped for one day. Just like this pattern, these ASCs had worked for 60 days from February 1, 2016 to April 1, 2016. ASCs' influent and effluent were sampled after columns had worked for an hour. When water samples arrived at 100 mL, get out of water samples through the Whatman glass fiber filters ($0.22 \mu\text{m}$) and put in 4°C freezer. This process was deemed to a complete sampling process.

The sorption experiment

The kinetics of sorption

The kinetics of sorption determine the rate of SMX and TMP removal from water. In the sorption dynamics experiment, with the solid: solution ratio (1:50 for SMX and 1:100 for TMP), weigh 5 g and 2.5 g clay ceramsites and put them in 500 mL ground-glass conical flask packed up with tinfoil to prevent the photodegradation. The initial solution concentration is $1 \text{ mg} \cdot \text{L}^{-1}$. All the samples were incubated at $25 \pm 1^\circ\text{C}$, being orbitally shaken at 150 rpm for 100 h in the dark. Grab samples with 1 mL injection syringes and filter samples through the Whatman glass fiber filters ($0.22 \mu\text{m}$) at 2 min, 5 min, 10 min, 15 min, 30 min, 1 h, 2 h, 4 h, 8 h, 12 h, 24 h, 28 h, 32 h, 36 h, 48 h, 60 h, 72 h, 84 h, 100 h.

The isotherm sorption experiment

In the isotherm sorption experiment, 50-mL amber EPA vials equipped with a polytetrafluoroethylene-lined screw caps was filled with 0.25 g (0.5 g) clay ceramsites and spiked with 25 mL TMP (SMX) concentration levels: 10, 20, 50, 80, 100, 200, 400, 600, 800 ppb. Blank control samples were also done. All the samples were also incubated at $25 \pm 1^\circ\text{C}$ while being orbitally shaken at 150 rpm for 100 h for in the dark. After incubation, all samples were centrifuged at 3000 rpm for 15 min, extracted with 1 mL injection syringes and filtered through the Whatman glass fiber filters ($0.22 \mu\text{m}$).

Analytical methods

Table S1 The gradient elution program

time/min	the mobile phase A	the mobile phase B
0	10%	90%
4	90%	10%
5	90%	10%
5.5	10%	90%
7	10%	90%

A represents Milli-Q water added 0.1% formic acid. B represents acetonitrile

Table S2 The antibiotics working parameter in mass spectrum

sulfonamides	precursor ion $/(m \cdot z^{-1})$	product ion $/(m \cdot z^{-1})$	cone voltage /v	collision energy /eV	dwel time /s
SMX	254.1	156	46.0	28.0	0.195
TMP	291.4	123	40.0	22.0	0.235

Table S3 The element analysis results of volcanics, clay cermisites, silty clay, coarse medium sands

	SiO ₂ /%	Al ₂ O ₃ /%	MgO /%	CaO /%	Na ₂ O /%	K ₂ O /%	Fe ₂ O ₃ /%	MnO /%	ZnO /%	CuO /%	others/ %
Clay ceramsites	56.28	15.78	0.76	9.29	0.09	2.25	15.38	0.13	0.03	0.01	0.10
Silty clay	71.48	9.72	1.43	6.71	1.00	2.86	5.50	0.09	0.01	0	1.20
Medium-coarse sands	79.32	9.52	0.36	1.87	1.42	4.66	2.19	0.05	0	0	0.61

The kinetics of sorption result

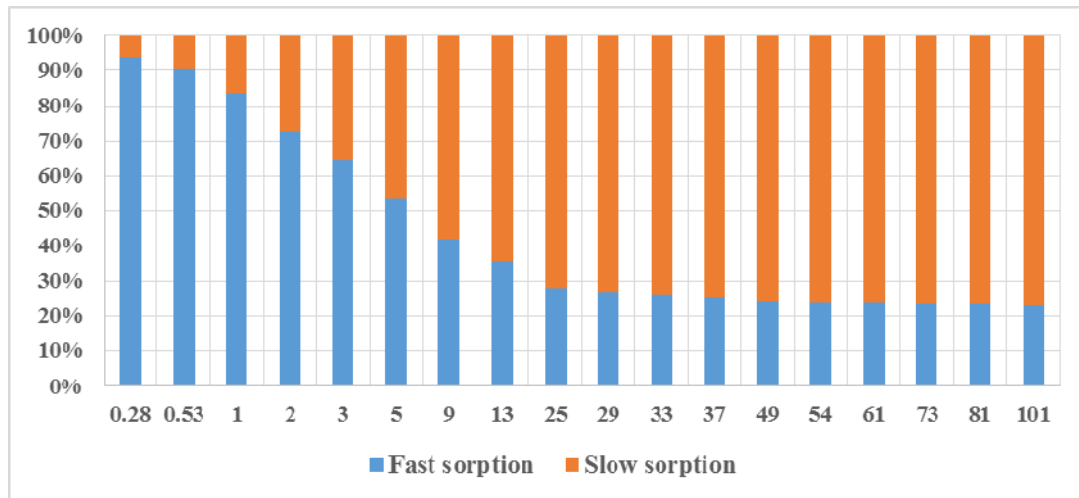


Fig. S1 The contribution of fast and slow sorption on SMX

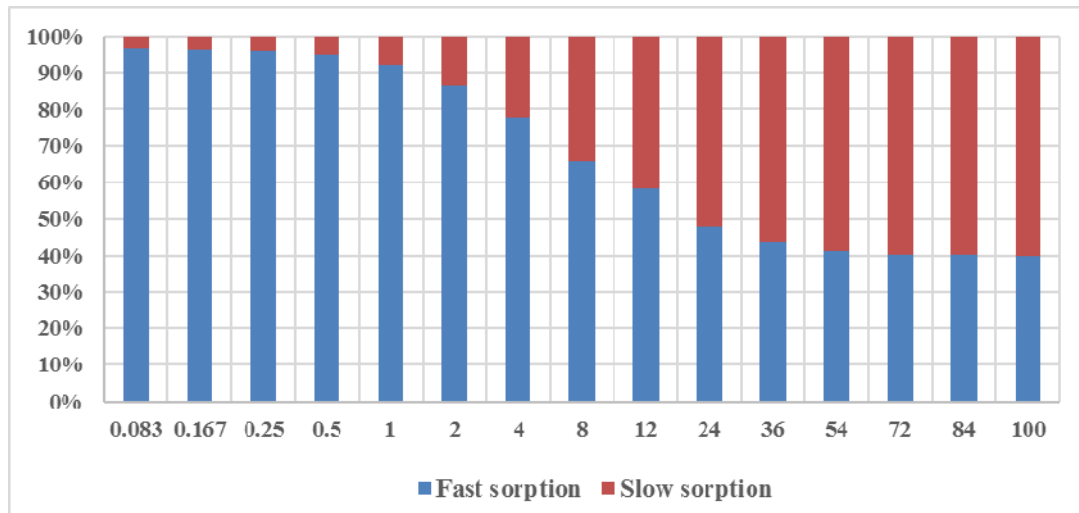


Fig. S2 The contribution of fast and slow sorption on TMP