

Supporting information

1 Field drilling and hydrogeological test

Ten sampling points were arranged to drill borehole cores, and the location and elevation of each borehole were accurately determined by real-time Global Positioning System (GPS). The construction of the groundwater monitoring wells followed the specifications of the Chinese Code of Practice for the Construction of Groundwater Monitoring Wells (DZ/T 0270—2014) (Appendix Technical Guide 2). The groundwater levels measured prior to sampling and records the depth to groundwater at elevations ranged from 740.60 to 739.52 m. Table S1 shows the field testing of water quality parameters at the site using a calibrated multiparameter probe (HachHQ300).

A total of three depth-reduced pumping tests were conducted, with the hydrometer TD-Diver automatically monitoring water level changes. The hydrogeologic parameters of the aquifer were solved using the analytical geometry of the is formula, and the results are shown in Tables S2–S4. Tracer tests using KBr as a tracer resulted in a longitudinal dispersion coefficient of 0.47 m²/h and a longitudinal dispersion degree of 3.92 m for the aquifer.

Table S1 Simultaneous field testing of water quality parameters without acidification using a calibrated multiparameter probe (HachHQ300)

Well	pH				TDS/(mg·L ⁻¹)				Conductivity/(uS·cm ⁻¹)				Do/(mg·L ⁻¹)				Fe ²⁺ /(mg·L ⁻¹)			Sulfide/(μg·L ⁻¹)		
	1	2	3	Average	1	2	3	Average	1	2	3	Average	1	2	3	Average	1	2	Average	1	2	Average
MZ01	5.04	5.22	5.19	5.15	2353.0	2392.0	1813.5	2186.2	2893	2963	2181	2679	1.77	2.47	1.14	1.79	4.80	2.67	6.408	8	—	—
MZ02	3.48	4.18	3.78	3.81	3016.0	3139.5	2041	2732.2	3654	3821	2482	3319	0.92	2.78	2.48	2.06	15.50	2.90	22.475	28	—	—
MZ03	3.41	3.53	2.98	3.31	3295.5	3256.5	1488.5	2680.2	4044	4041	1798	3294.333333	1.69	4.17	1.48	2.45	19.10	3.70	35.335	7	—	—
MZ04	4.58	4.35	5.63	4.85	2752.5	3009.5	2275	2679.0	3439	3774	2789	3334	1.12	1.95	1.28	1.45	18.50	1.50	13.875	3	—	—
MZ05	5.93	5.91	6.13	5.99	2513.0	2548.0	2561	2540.7	3260	3159	3154	3191	0.69	3.48	2.35	2.17	0	1.30	0	26	—	—
MZ06	3.76	3.56	3.83	3.72	2301.0	2353.0	1963	2205.7	2811	2876	2365	2684	3.60	4.49	2.85	3.65	0.87	1.61	0.70035	35	—	—
MZ07	5.51	5.53	5.88	5.64	2673.0	2990.0	2561	2741.3	3585	3765	3146	3498.666667	1.17	2.28	1.16	1.54	2.50	2.73	3.4125	26	—	—
MZ08	5.76	5.01	5.99	5.59	2632.5	2574.0	2496	2567.5	3299	3287	3067	3217.666667	0.66	0.70	1.04	0.80	2.60	2.75	3.5750	117	—	—
MZ09	6.05	6.24	6.05	6.11	3711.5	4095.0	3510	3772.2	4607	5143	4285	4678.333333	1.09	1.19	1.30	1.19	0.59	6.80	2.0060	36	—	—
MZ10	3.42	3.47	3.39	3.43	3165.5	2146.0	3185	2832.2	3755	3728	3766	3749.666667	4.00	3.37	0.91	2.76	1.07	0.24	0.1284	22	—	—
MZ11	6.60	6.22	—	6.41	1105.0	1118.0	—	1111.5	1369	1411	—	1390	0.58	0.98	—	0.78	1.26	0.46	0.2898	72	—	—

Groundwater pH, TDS(total dissolved solids), and Do(dissolved oxygen) were obtained for the site. The concentrations of dissolved Fe(II) were determined by ferrozine method [1]. The pH of groundwater at the site was acidic and the TDS values were high, indicating that the groundwater at the site was contaminated.

Table S2 Hydrogeological parameters of aquifers obtained from pumping tests

Experimental group	Observation well	Flow rate/ ($\text{m}^3 \cdot \text{d}^{-1}$)	r/m	S_0/m	Aquifer thickness/ m	Hydraulic conductivity/ ($\text{m}^2 \cdot \text{d}^{-1}$)	Permeability coefficient/ ($\text{m} \cdot \text{d}^{-1}$)	Elasticity of water delivery
First pumping	MZ01	3.1418	4.0150	0.0780	2.50	3.2070	1.2828	0.8753
	MZ03	3.1418	5.0750	0.0390	2.50	6.4140	2.5656	6.3752
	MZ04	3.1418	4.4750	0.0350	2.50	7.1470	2.8588	2.3555
Second pumping	MZ01	4.9371	4.0150	0.1750	2.50	2.2462	0.8985	1.0033
	MZ02	4.9371	2.6500	0.1400	2.50	2.8077	1.1231	27.9875
	MZ03	4.9371	5.0750	0.2000	2.50	1.9654	0.7862	1.9780
	MZ04	4.9371	4.4750	0.1600	2.50	2.4568	0.9827	2.7284
Third pumping	MZ01	3.8400	4.0150	0.0925	2.50	3.3052	1.3221	1.2138
	MZ02	3.8400	2.6500	0.1200	2.50	2.5478	1.0191	5.8048
	MZ03	3.8400	5.0750	0.0900	2.50	3.3970	1.3588	8.9688
	MZ04	3.8400	4.4750	0.0870	2.50	3.5142	1.4057	2.6323

r represents the distance from the observation well to the pumping well; S_0 refers to the depth of water level drop in the observation well during the pumping test. The standard curve comparison method was used in this test. The analytical geometry of the formula was utilized to solve the hydrogeological parameters of the aquifer. The permeability coefficients of the aquifer at the site ranged from 0.9×10^{-3} to 3.3×10^{-3} cm/s, which is close to the reference value of the permeability coefficient of fine sand.

Table S3 Hydrogeological parameter values

Parameter	$K_x/(\text{m} \cdot \text{d}^{-1})$	$K_y/(\text{m} \cdot \text{d}^{-1})$	$K_z/(\text{m} \cdot \text{d}^{-1})$	Porosity	S_s	S_r	α/m^{-1}	n
Miscellaneous fill	0.0864	0.0864	0.0864	0.5	1	0.12	1.2	3
Silty fill	0.1	0.1	0.01	0.05	1	0.12	1.2	3
Pebble-gravel layer	1	1	0.1	0.1	—	—	—	—
Bedrock	4	4	0.4	0.1	—	—	—	—

K_x is the hydraulic conductivity in x direction; K_y is the hydraulic conductivity in y direction; K_z is the hydraulic conductivity in z direction; S_s is the maximum saturation, applied to all empirical models; S_r is the residual saturation, applied to all empirical models; α and n are fitting parameters.

Table S4 Reactive solute transport parameter values

Parameter	Diffusion coefficient/ ($10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$)	Longitudinal dispersivity/ m	Transverse dispersion/ m	Reaction coefficient (Zn)	Retention coefficient (Zn)/(10^{-4} s^{-1})
Miscellaneous fill	200	1	0.2	1×10^{-5}	10
Silty fill	200	1	0.2	1×10^{-5}	10
Pebble-gravel layer	200	1	0.2	1×10^{-5}	10
Bedrock	2300	100	20	1×10^{-5}	10

2 Geophysical exploration method

The complex geological structure of the study area is clarified according to the Technical Regulations of Resistivity Profiling Method (DZ/T 0073—2016) and Technical Regulations of Geological Radar Exploration in Hydropower Engineering (NB/T 10133—2019) combined with the high-density electrical method and the geological radar measurement based on high-frequency electromagnetic wave theory. There are 9 high-density survey lines and 16 geodetic radar sidings arranged in the study area (Figure S1), and the area contains several boreholes, which is favorable for comparison and verification. By comparing the high-density electrical method results and drill core results, the main stratigraphic layers were identified from top to bottom as miscellaneous fill, silty fill, transition layer, pebble-gravel layer, and bedrock, and the subsurface wall of the study area was inferred and identified. Based on the characteristics of the georadar profiles, the main anomalies such as non-pressure-bearing zones, suspected walls and water-rich layers were identified.

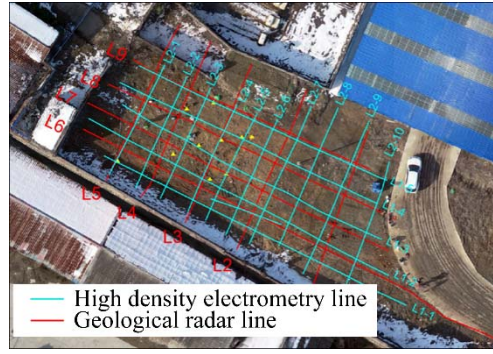


Figure S1 High density electrical and geo-radar wiring diagram

3 Theoretical mathematical models

In constructing a three-dimensional groundwater numerical model, we focus on the coupled saturated and unsaturated zone processes in the soil groundwater system. In controlling the hydraulic flow equations, with the head as the main variable, the governing equations of water flow in three-dimensional variably saturated porous media are as follows:

$$S_0 S_w(H) \frac{\partial H}{\partial t} + \phi \frac{\partial S_w(h)}{\partial t} + \nabla V = Q \quad (1)$$

$$V = k_{rw}(S_w) K [\nabla h + \chi e] \quad (2)$$

where S_0 is the water storage coefficient; S_w is the degree of saturation (in the unsaturated zone S_w is a function of head, $0 < S_w \leq 1$, and in the saturated zone $S_w = 1$); h is the hydraulic head of groundwater at the monitoring point; t is the time; ϕ is the dimensionless porosity; ∇V is the flow velocity gradient; q is the source-sink term of the flow system; k_{rw} is the relative permeability (in the unsaturated zone k_{rw} is a function of saturation, calculated from the van Genuchten-Mualem model, and in the saturated zone k_{rw} is 1); K is the permeability coefficient of the medium; V is the Darcy flow velocity; ∇h is the dimensionless hydraulic gradient; χ is the buoyancy coefficient, which represents the density effect of the fluid; e is the unit normal vector.

Under the solute transport section, we consider reactive solute transport and focus mainly on the effects of the reaction coefficient (λ) and retention coefficient (R) on solute transport. The three-dimensional saturated-unsaturated solute transport control equation for the target pollutant is as follows:

$$\frac{\partial}{\partial x_i} \left(D_{ij} \frac{\partial c}{\partial x_j} \right) - V_i \frac{\partial c}{\partial x_i} = \phi S_w R \left(\frac{\partial c}{\partial t} + \lambda c \right) + Q(c - c^*) \quad (3)$$

$$R = 1 + \frac{\rho_s (1 - \phi) K_d}{\phi S_w} \quad (4)$$

where c is the pollutant source concentration; c^* is the pollutant concentration infiltrated into the groundwater; D_{ij} is the hydrodynamic dispersion coefficient; x_i and x_j are the spatial coordinates; R is the retention coefficient, characterizing the adsorption capacity of the soil, and it is dimensionless; ρ_s is the soil particle density; K_d is the partition coefficient; λ is the reaction coefficient. In this paper, we mainly consider the reaction process of HMs released from soil to HMs in groundwater.

Reference

- [1] STOOKEY L L. Ferrozine—A new spectrophotometric reagent for iron [J]. Analytical chemistry, 1970, 42: 779–781.