A Computational Framework for Design and Optimization of Risk-Based Soil and Groundwater Remediation Strategies

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Text S1. The geochemical and biogeochemical reactions that affect As reactive transport in the model

(1) Microbially mediated reduction and release of Fe(III)

Microbially mediated Fe(III) reduction and consequent release of adsorbed As from the iron oxide surfaces into groundwater are generally considered an important As reactive transport process [1-3]. The reaction is described as below:

$$\frac{1}{4}CH_2O + 2H^+ + Sediment - Fe(OH)_3 - As(V) \xrightarrow{k_1} As(V) + Fe^{2+} + \frac{1}{4}CO_2 + \frac{11}{4}H_2O \tag{S1}$$
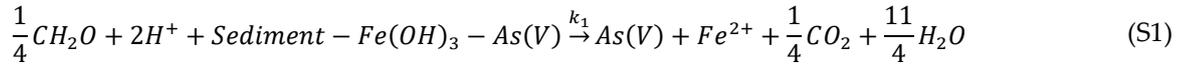
where Sediment-Fe(OH)$_3$-As (V) denotes the As sorbed on ferrihydrite surfaces in sediments. The chemical formula of Fe(OH)$_3$ represents ferrihydrite. The abbreviations of CH$_2$O and As(V) denote the dissolved organic carbon (DOC) and arsenate, respectively.

The kinetic rate controlling Fe(III) reduction and subsequent As release was described using the Monod expression [4].

$$R_1 = k_1 C_{Fe} \frac{C_{DOC}}{K_{DOC} + C_{DOC}} \tag{S2}$$

Here, k_1 is the rate constant, C_{Fe} is the concentrations of ferrihydrite, C_{DOC} is the concentrations of DOC, K_{DOC} is the half saturation constants ewith respect to DOC.

(2) Fe (II) oxidation

Fe (II) oxidation was described using the following reaction and rate expression [5]:

$$Fe^{2+} + \frac{1}{4}O_2 + \frac{5}{2}H_2O \xrightarrow{k_2} Sediment - Fe(OH)_3 - As(V) + 2H^+ \tag{S3}$$
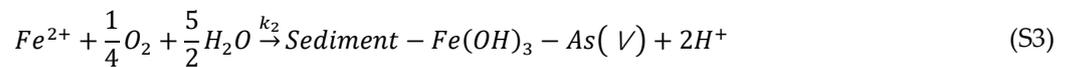
$$R_2 = k_2 C_{Fe^{2+}} C_{O_2} \tag{S4}$$

Here, k_2 is the rate constant, C_{Fe2+} is concentrations of Fe (II), C_{O2} is concentrations of solved oxygen (DO).

(3) Aerobic respiration

Aerobic respiration is a main process that consumes DO and DOC in groundwater, which indirectly affects the Fe(III) reductive dissolution and As release. The aerobic respiration can be described as [6]:

$$CH_2O + O_2 \xrightarrow{k_3} H_2O + CO_2 \tag{S5}$$
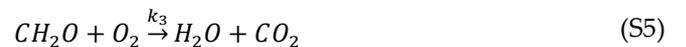
$$R_3 = k_3 \frac{C_{DOC}}{K_{DOC} + C_{DOC}} \frac{C_{O_2}}{C_{O_2} + K_{O_2}} \tag{S6}$$

Here, k_3 is the rate constant, C_{O2} and C_{DOC} are the concentrations of DO and DOC, K_{DOC} and K_{O2} are the half saturation constants with respect to DOC and DO, respectively.

(4) DOC production from particulate organic carbon (POC) transformation

The following reaction and rate expression were used to describe the process of DOC production from POC [5].

$$POC \xrightarrow{\alpha DOC} DOC(CH_2O) \tag{S7}$$

$$R_4 = \alpha DOC(K_{d,DOC}C_{DOC} - C_{POC}) \tag{S8}$$

Here, α_{DOC} is the first-order mass transfer coefficients for DOC, $K_{d,DOC}$ is distribution coefficients of DOC between groundwater and soil particle, C_{DOC} is concentration of DOC, POC is particulate organic carbon.

Table S1. Hydrogeological parameters used in this study.

Parameters	Porosity	K (m/d)
Fill layer	0.4	1
Sand layer	0.358	0.8
Silty layer	0.3	0.05
Bed Rock layer	0.2	0.001

Table S2. Reaction parameters used in this study.

Parameters	Unit	Value
k_1	1/s	[5] 2.78×10^{-8}
K_{DOC}	mol/L	[4] 2.89×10^{-4}
k_2	L/(mol·h)	[6] 1500
k_3	mol/(L·s)	[4] 6.47×10^{-10}
K_{O2}	mol/L	[4] 1.65×10^{-4}
α_{DOC}	1/h	[5] 2×10^{-4}
$K_{d,DOC}$	L/g	[6] 5×10^{-2}

Table S3. Boundary conditions of chemical species in this study.

Parameters	Boundary condition	
(mol/L)	Shaibei River	Rainfall
As(V)	4.64×10^{-8}	0.00
DO	1.6×10^{-4}	1.297×10^{-3}
DOC	4.76×10^{-4}	0.00
Fe(II)	0.00	0.00
CO2	3.3×10^{-2}	3.3×10^{-2}
pH	7.25	6.00

Table S4. Optimized RFR hyperparameter values.

Model hyperparameters	Optimum hyperparameter value	
	Groundwater	Soil
n_estimators	400	1000
min_impurity_decrease	0	0
max_features	auto	auto
criterion	mae	mse
min_samples_split	3	2

Table S5. The specific parameters of SCE algorithm in this study.

Parameter	Value
P_{comp}	20
n_{max}	200,000
k_{stop}	100
P_{cento}	0.01

Table S6. R^2 and NSE of the RFR model under different remediation requirement.

Remediation requirement	R^2	NSE
Groundwater	0.9998	0.9995
Soil	0.9637	0.9965
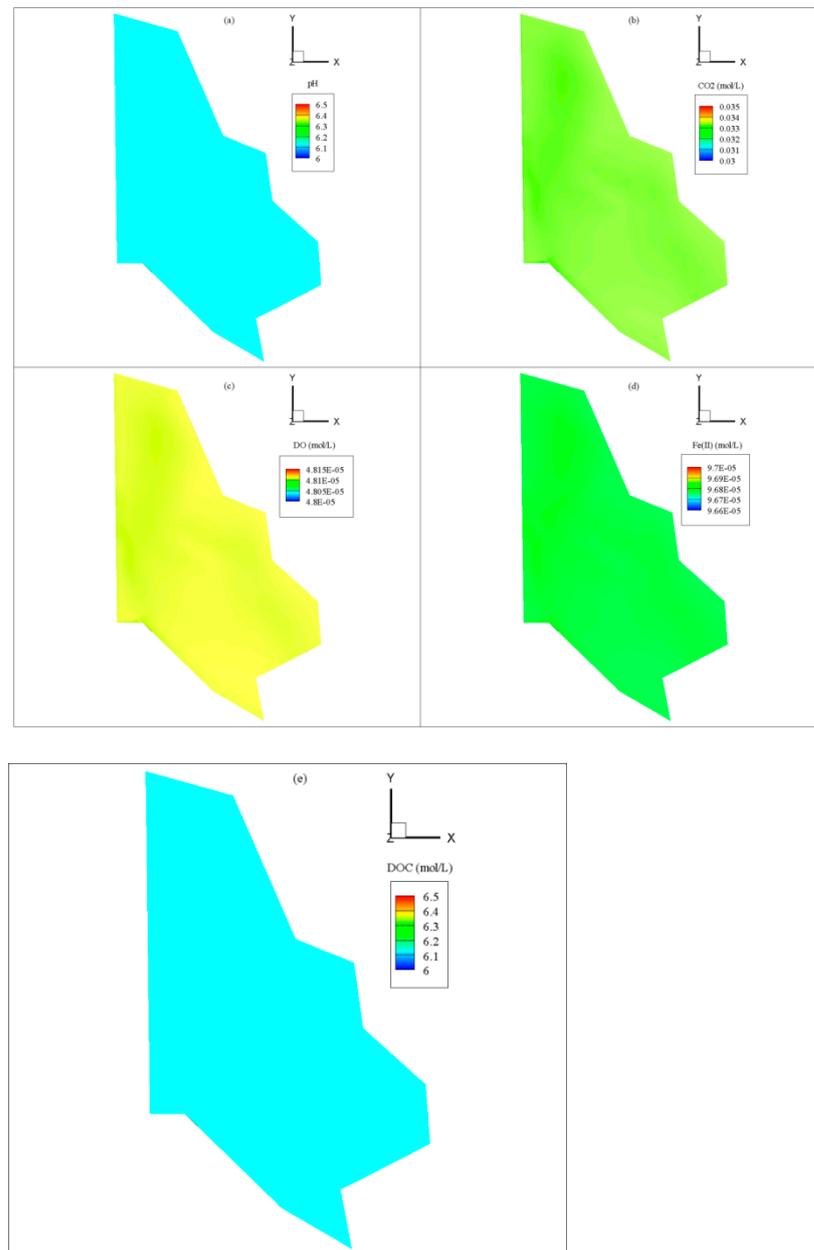
**Figure S1.** The initial distribution of pH(a), CO_2(b), DO(c), Fe(II)(d) and DOC(e).
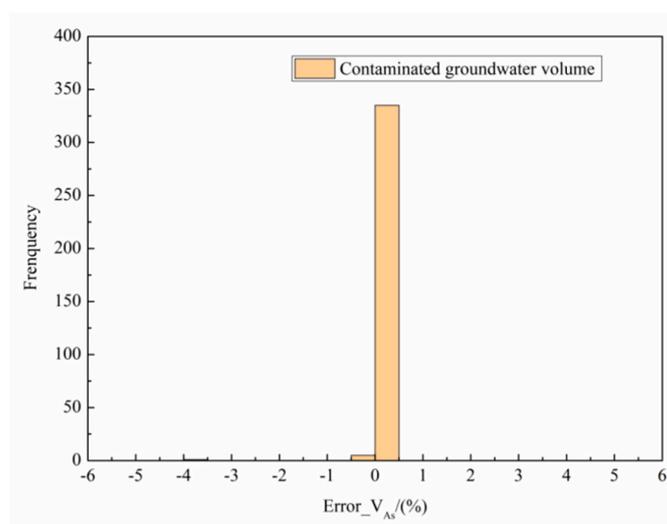
Figure S2. The performance of RFR model under groundwater remediation requirement. Error_V_{As}=(V_{As_RFR}-$V_{As\_Process}$)/V_{Water_total}. Here, V_{As_RFR} and $V_{As\_Process}$ are the volumes of groundwater with As concentration exceeding 10 ug/L obtained from RFR model and process-based model, respectively. V_{Water_total} is the total contaminated groundwater volume with As concentration exceeding 10 ug/L.
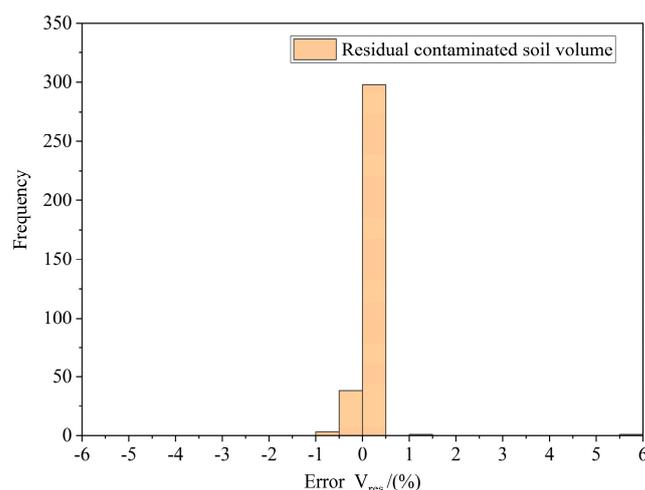

Figure S3. The performance of RFR model under soil remediation requirement. Error_V_{res}=(V_{res_RFR}-$V_{resl\_Process}$)/V_{As_total}. Here, V_{res_RFR} and $V_{res\_Process}$ are the residual contaminated soil volumes obtained from RFR model and process-based model, respectively; V_{As_total} is the total contaminated soil volume with As concentration exceeding 60 mg/kg.

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