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RESEARCH ARTICLE

# Modeling soil pH dynamics with distinct buffering mechanisms: insights from two purple soils

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## SUPPLEMENTARY MATERIALS

**Table S1** Process description used in the VSD+ model to predict the soil solution chemistry

Formula	No.
$[\text{HCO}_3^-] = \frac{K_1 \cdot K_H \cdot p_{\text{CO}_2}}{[\text{H}]}$	(1)
$[\text{RCOO}^-] = \frac{m \cdot \text{DOC} \cdot K_{\text{org}}}{K_{\text{org}} + [\text{H}]}$	(2)
$X_{\text{ad}} = \frac{X_{\text{admax}} \cdot [X]}{X_{\text{half}} + [X]}$ $X = \text{SO}_4^{2-} \text{ or } \text{H}_2\text{PO}_4^-$	(3)
$\frac{d}{dt} (\theta \cdot z \cdot [X] + \rho \cdot z \cdot X_{\text{ad}}) = X_{\text{in}} - Q \cdot [X]$ $X = \text{SO}_4^{2-} \text{ or } \text{H}_2\text{PO}_4^-$	(4)
$\frac{d}{dt} (\theta \cdot z \cdot [\text{NH}_4^+]) = \text{NH}_{4,\text{in}} - \text{NH}_{4,\text{upt}} - N_{\text{im}} - N_{\text{ni}}$	(5)
$\frac{d}{dt} (\theta \cdot z \cdot [\text{NO}_3^-]) = \text{NO}_{3,\text{in}} + N_{\text{ni}} - \text{NO}_{3,\text{upt}} - N_{\text{de}}$	(6)
$\frac{d}{dt} (\theta \cdot z \cdot [\text{BC}] + \rho \cdot z \cdot \text{CEC} \cdot E_{\text{BC}}) = \max(\text{BC}_{\text{in}} + z \cdot \text{BC}_{\text{wea}} - \text{BC}_{\text{upt}}, Q \cdot [\text{BC}]_{\text{min}})$	(7)
$E_{\text{H}}/E_{\text{BC}} = k_{\text{HBc}} \cdot [\text{H}^+]/[\text{BC}^{2+}]^{1/2}$	(8)
$E_{\text{Al}}/E_{\text{BC}} = k_{\text{AlBc}} \cdot [\text{Al}^{3+}]^{1/3}/[\text{BC}^{2+}]^{1/2}$	(9)
$E_{\text{BC}} + E_{\text{Al}} + E_{\text{H}} = 1$	(10)
$[\text{Al}^{3+}] = K_{\text{AlOx}} \cdot [\text{H}^+]^3$	(11)
$[\text{H}^+] = ([\text{SO}_4^{2-}] + [\text{NO}_3^-] + [\text{HCO}_3^-] + [\text{H}_2\text{PO}_4^-] + [\text{Cl}^-]) + [\text{RCOO}^-] - ([\text{BC}^{2+}] + [\text{Na}^+] + [\text{Al}^{3+}] + [\text{NH}_4^+])$	(12)

Note: Nos. (1)–(6)  $K_1$  is the first dissociation constant,  $K_H$  is Henry's constant and  $p_{\text{CO}_2}$  represents the partial pressure of  $\text{CO}_2$  in the soil solution (in atm.);  $[\text{H}]$  is the concentration of hydrogen ions in soil solution;  $\text{DOC}$  is the concentration of dissolved organic carbon (in  $\text{g C m}^{-3}$ ), and  $m$  is the total concentration of organic compounds per  $\text{g C}$  also referred to as the concentration of functional groups (eq  $\text{g}^{-1} \text{C}$ ) and  $K_{\text{org}}$  is the dissociation constant of organic anions ( $\text{RCOO}^-$ )<sup>[1]</sup>, which was included as  $(pK_{\text{org}} = a + b \times \text{pH} - c \times \text{pH}^2)$  with  $a = 0.96$ ,  $b = 0.9$  and  $c = 0.039$ ;  $X_{\text{in}}$  refers to the input of element  $X$  by atmospheric deposition and fertilizer input, while  $X_{\text{upt}}$  is element uptake by plants;  $N_{\text{im}}$ ,  $N_{\text{ni}}$  and  $N_{\text{de}}$  are the immobilization rate, nitrification rate and denitrification rate, respectively;  $[X]$  indicates the concentration of element  $X$  in soil solution;  $X_{\text{ad}}$  is the adsorbed amount of element  $X$  by soils;  $X_{\text{admax}}$  is the maximum adsorption capacity of the soil ( $\text{meq kg}^{-1}$ ), and  $X_{\text{half}}$  is the half-saturation constant ( $\text{meq L}^{-1}$ );  $\theta$  is the volumetric water content of the soil ( $\text{m}^3 \cdot \text{m}^{-3}$ );  $z$  is the thickness of the soil compartment (m);  $Q$  denotes the runoff (precipitation surplus) ( $\text{m} \cdot \text{yr}^{-1}$ ). No. (7)  $\text{BC}$  includes  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{K}^+$ , while  $\text{Na}$  uptake is neglected;  $\text{BC}_{\text{wea}}$  indicates soil weathering rates and  $[\text{BC}]_{\text{min}}$  ( $\text{eq m}^{-3}$ ) is a prescribed minimum concentration in soil solution. Nos. (8)–(11)  $E_X$  is the equivalent fraction of ion  $X$  at the exchange complex;  $k_{\text{HBc}}$  and  $k_{\text{AlBc}}$  are the selectivity constants for the H-BC and Al-BC, respectively, while  $K_{\text{AlOx}}$  is the Al equilibrium constant. No. (12) Soil pH is computed with by the charge balance principle where  $\text{H}^+$  is determined by the sum of all anions minus cations.

**Table S2** Localization of model input parameters used in the VSD+ model

Parameters	Description	Unit	Beibei	Jiangjin
thick	Soil depth	m	0.20	0.20
Bulk density	Soil bulk density	$\text{g} \cdot \text{cm}^{-3}$	1.38	1.10
Clay_ct	Clay content	%	26.80	21.70
pCO <sub>2</sub> fac	Multiplier of air CO <sub>2</sub> pressure (0.4 mbar) for the partial CO <sub>2</sub> pressure in the soil solution	–	4.00	10.00
CEC	Soil cation exchange capacity	$\text{meq kg}^{-1}$	239.79	295.00
parentCa	Initial CaCO <sub>3</sub>	%	0.30	0
Cpool_0	Initial C pool in soil	$\text{g} \cdot \text{m}^{-2}$	3808.05	3588.75
CNrat_0	Initial C:N ratio in soil	$\text{g} \cdot \text{g}^{-1}$	10.86	7.84
Ca_we	Ca weathering rate	$\text{keq ha}^{-1} \cdot \text{yr}^{-1}$	5.30	5.30
K_we	K weathering rate	$\text{keq ha}^{-1} \cdot \text{yr}^{-1}$	1.73	1.73
Mg_we	Mg weathering rate	$\text{keq ha}^{-1} \cdot \text{yr}^{-1}$	0.40	0.40
Na_we	Na weathering rate	$\text{keq ha}^{-1} \cdot \text{yr}^{-1}$	0.20	0.20
SO <sub>4</sub> half	Half-saturation constant for SO <sub>4</sub> <sup>2-</sup>	$\text{meq L}^{-1}$	0.41	0.41
SO <sub>4</sub> admax	Maximum adsorption capacity of SO <sub>4</sub> <sup>2-</sup> by soil	$\text{meq kg}^{-1}$	0.83	0.83
PO <sub>4</sub> half	Half-saturation constant for H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	$\text{meq L}^{-1}$	0.41	0.41
PO <sub>4</sub> admax	Maximum adsorption capacity of H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> by soil	$\text{meq kg}^{-1}$	20.84	20.84
knit	Maximum nitrification rate	$\text{yr}^{-1}$	4.00	4.00
kdenit	Maximum denitrification rate	$\text{yr}^{-1}$	4.00	4.00
Nfix <sup>#</sup>	Nitrogen fixation	$\text{keq ha}^{-1} \cdot \text{yr}^{-1}$	2.14	0.36
Nupeff	Uptake efficiency of available N	–	0.92	0.92
Clf	Carbon litterfall flux to soil C pool	$\text{g} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$	274.74	178.58
Nlf	Nitrogen litterfall flux to soil N pool	$\text{g} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$	6.50	4.02
rf_miR	Reduction factor mineralization	–	2.34	2.62
rf_nit	Reduction factor nitrification	–	2.67	3.08
rf_denit	Reduction factor denitrification	–	0.03	0.02
KAIBC	Exchange constant Al versus BC	$(\text{meq L}^{-1})^{1/6}$	2.13*	-0.24*
KHBC	Exchange constant H versus BC	$(\text{meq L}^{-1})^{-1/2}$	3.01*	2.15*
KAl ox	Al equilibrium constant	$(\text{meq L}^{-1})^{-2}$	10.16*	7.01*

# The N fixation in paddy and upland soils, we used the latest fixed parameters of 30 and 5  $\text{kg} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$  in the VSD+ model, respectively<sup>[2]</sup>; \*Values are given as logarithmic data.

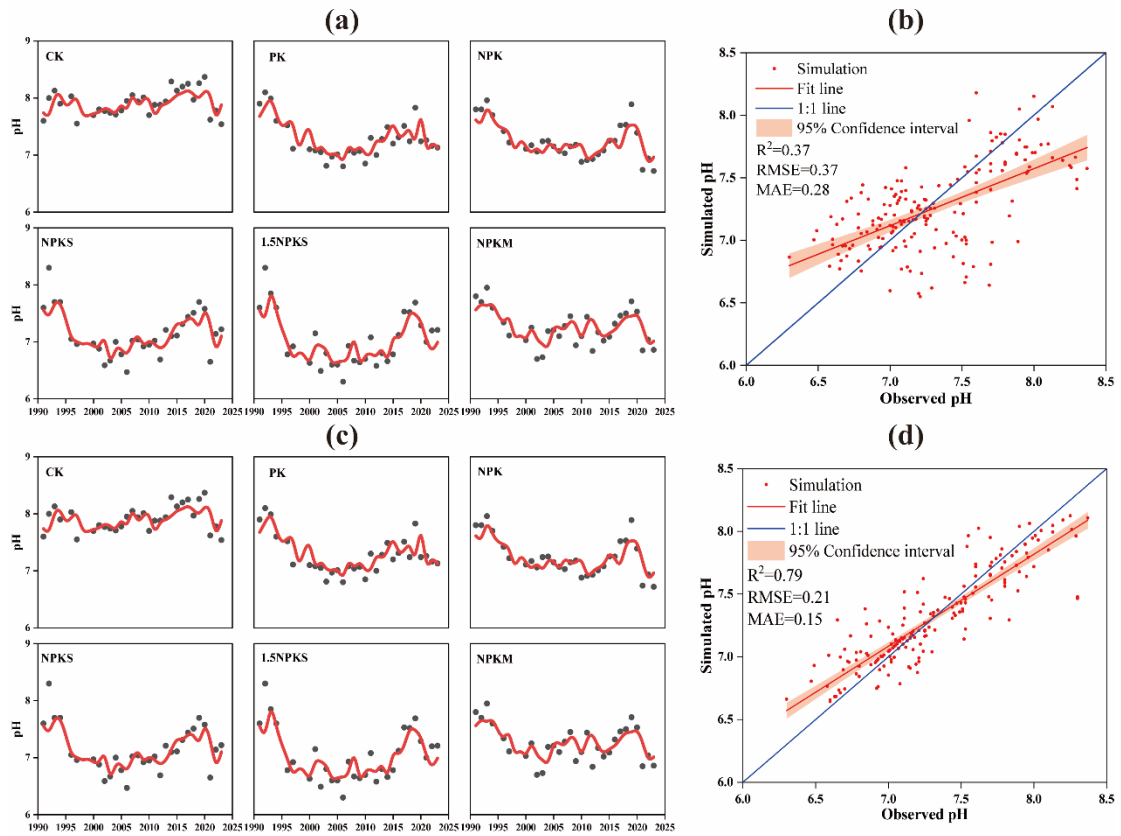
**Table S3** Average annual total nutrient inputs ( $\text{keq ha}^{-1}\cdot\text{yr}^{-1}$ ) of the Beibei (1991–2023) and the Jiangjin (2013–2023) sites

Treatment	$\text{NH}_4\text{-N}$	$\text{NO}_3\text{-N}$	$\text{H}_2\text{PO}_4\text{-P}$	BC	$\text{SO}_4\text{-S}$
Beibei					
CK	4.10	1.15	0	3.00	3.89
PK	4.10	1.15	0.88	5.22	5.21
NPK	11.80	8.86	0.88	5.22	5.21
NPKS	13.48	10.54	0.91	10.20	4.69
1.5NPKS	17.24	14.30	1.44	12.35	5.88
NPKM	13.37	10.43	1.39	11.87	5.21
Jiangjin					
CN	4.10	1.15	0.85	5.14	5.16
OP	12.00	9.06	0.85	5.14	5.16
FP	16.95	14.01	1.69	5.99	5.16

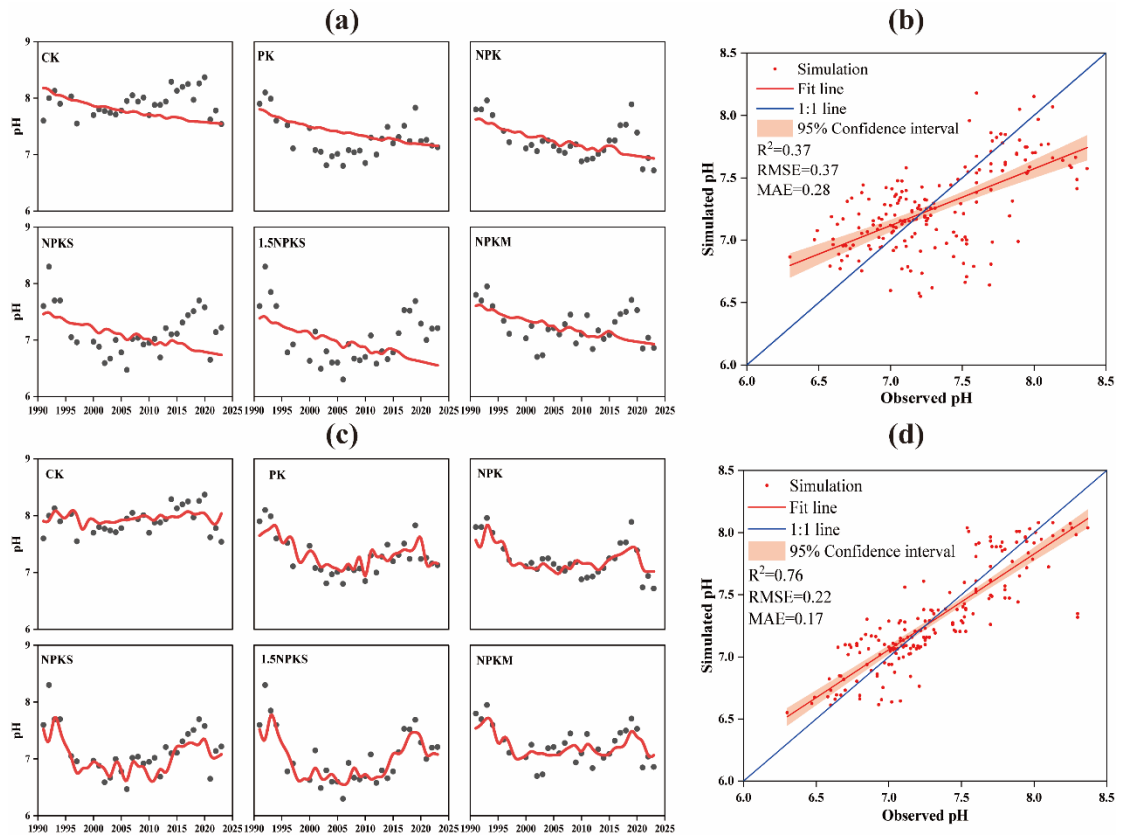
**Table S4** Selected variables for machine learning modelling at the Beibei (1991–2023) and Jiangjin (2013–2023) sites

Type	Variable	Unit	Beibei	Jiangjin
Climate	Mean annual temperature	°C	18.72	19.35
	Mean annual precipitation	m·yr <sup>-1</sup>	1.17	1.07
Nutrient management	N-input	eq m <sup>-2</sup>	1.84	1.91
	P-input	eq m <sup>-2</sup>	0.09	0.11
	K-input	eq m <sup>-2</sup>	0.44	0.13
	Ca-input	eq m <sup>-2</sup>	0.29	0.11
	Mg-input	eq m <sup>-2</sup>	0.07	0
	S-input	eq m <sup>-2</sup>	0.50	0.52
	N-uptake	eq m <sup>-2</sup>	1.41	1.32
	P-uptake	eq m <sup>-2</sup>	0.11	0.09
	K-uptake	eq m <sup>-2</sup>	0.51	0.50
	Ca-uptake	eq m <sup>-2</sup>	0.06	0.08
	Mg-uptake	eq m <sup>-2</sup>	0.10	0.11
Soil background information	S-uptake	eq m <sup>-2</sup>	0.14	0.08
	Soil background pH	–	7.60	4.90
	SOM	g·kg <sup>-1</sup>	25.32	24.77

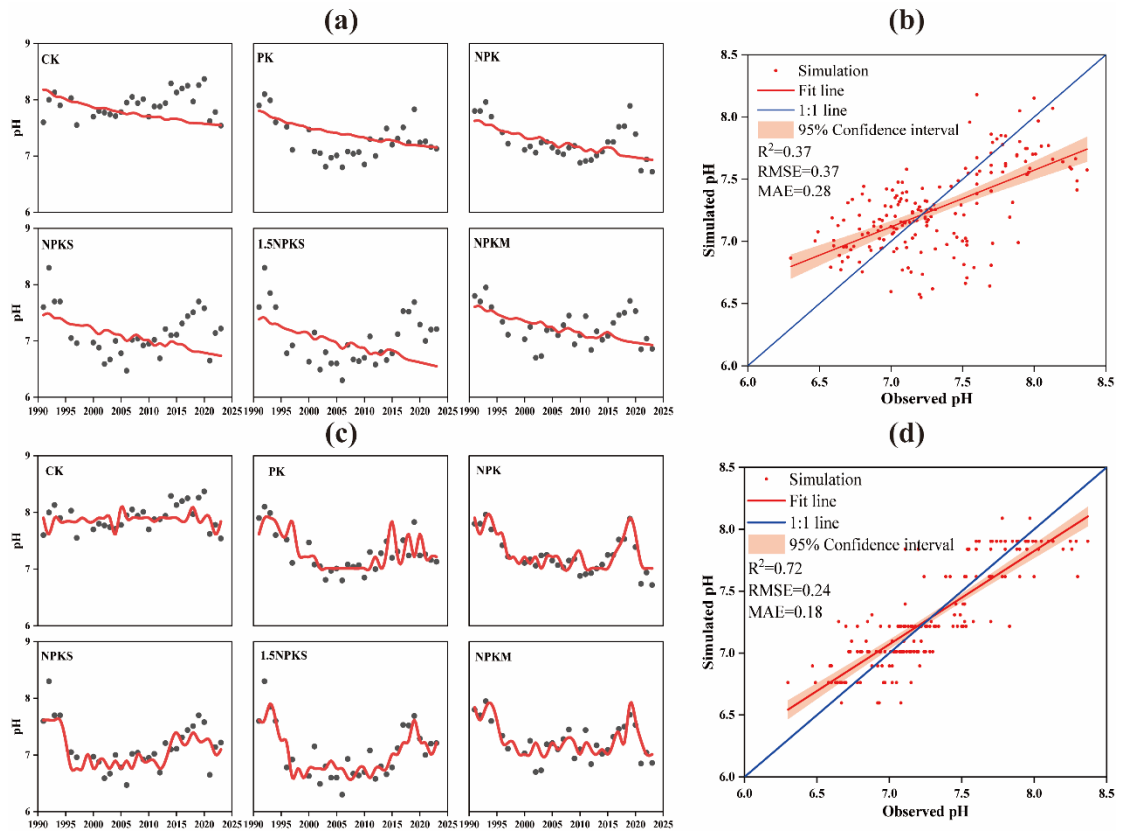
Note: Data for selected variables are averaged across all treatments at each site.



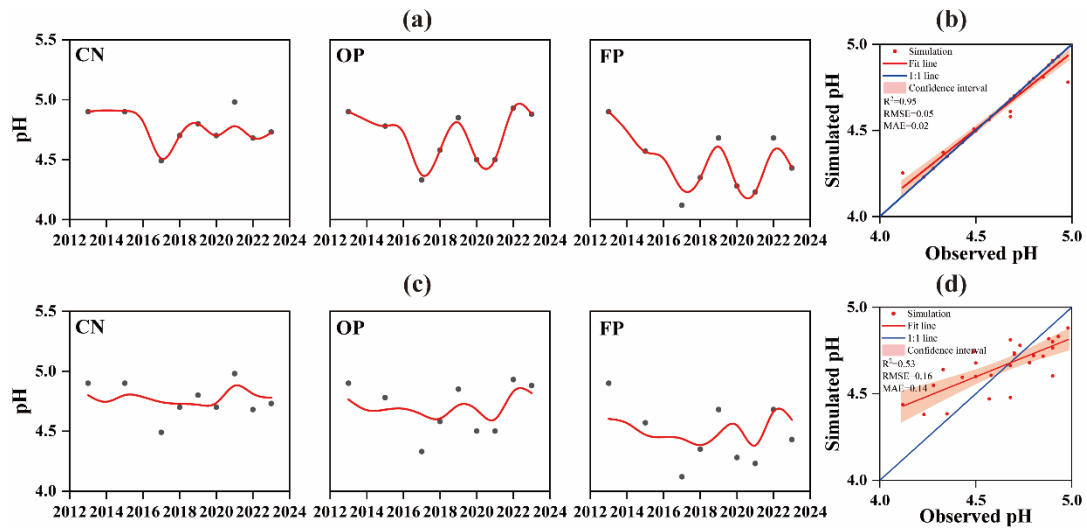
**Fig. S1** Comparison of the simulation and fitting performance of the VSD+ and SVM models on neutral purple soil. (a) Observed (dots) and simulated (lines) changes in pH and (b) the scatter plot under six treatments by the VSD+ model; (c) observed and simulated changes in pH and (d) the scatter plot under six treatments by the SVM model, respectively. CK, a control with no fertilizer; PK, mineral P and K, NPK, mineral N, P and K fertilizers; NPKS, mineral N, P and K plus straw; 1.5NPKS, 1.5 times mineral N, P and K plus straw; and NPKM, mineral N, P and K plus manure.



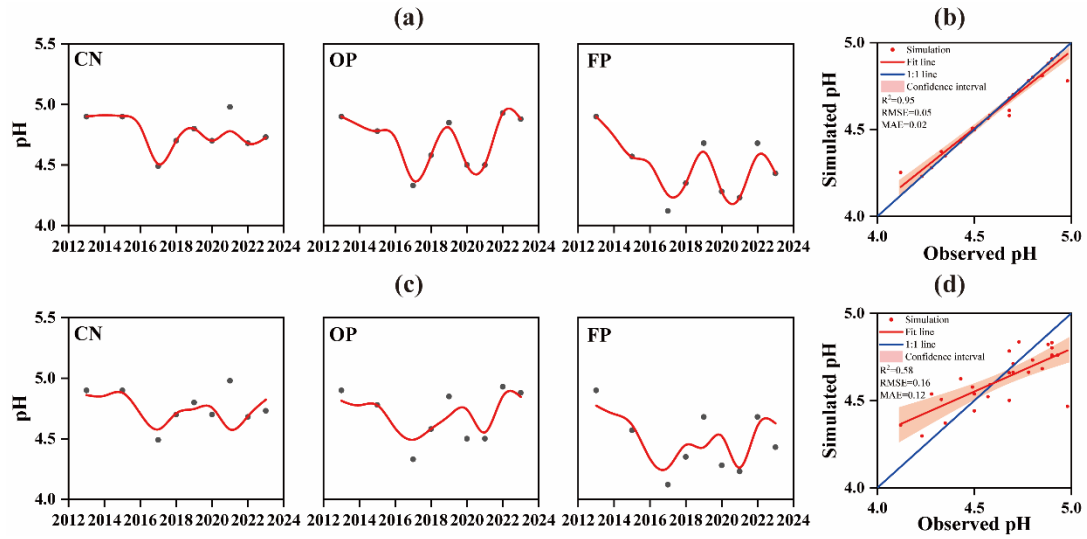
**Fig. S2** Comparison of the simulation and fitting performance of the VSD+ and XGB models on neutral purple soil. (a) Observed (dots) and simulated (lines) changes in pH and (b) the scatter plot under six treatments by the VSD+ model; (c) observed and simulated changes in pH and (d) the scatter plot under six treatments by the XGB model, respectively. CK, a control with no fertilizer; PK, mineral P and K, NPK, mineral N, P and K fertilizers; NPKS, mineral N, P and K plus straw; 1.5NPKS, 1.5 times mineral N, P and K plus straw; and NPKM, mineral N, P and K plus manure.



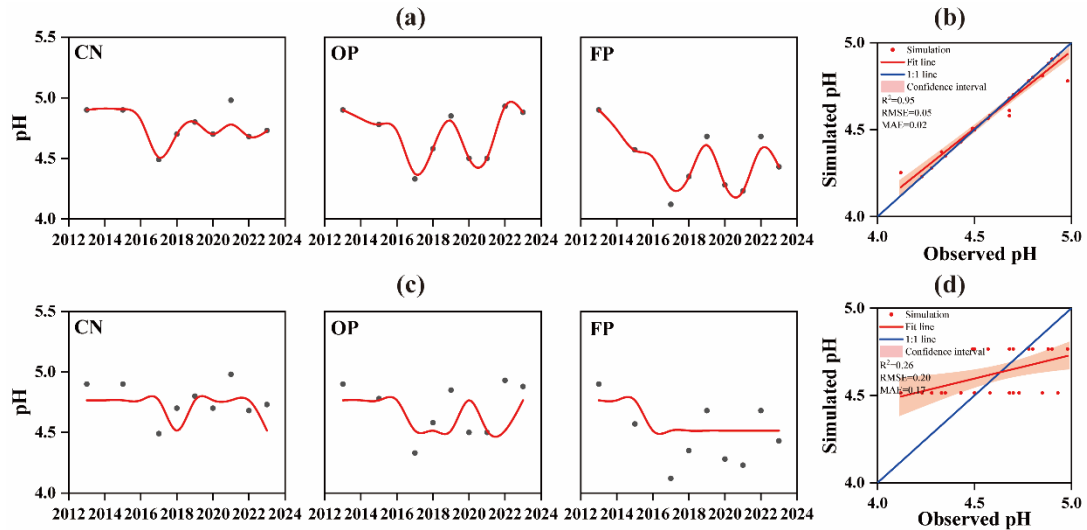
**Fig. S3** Comparison of the simulation and fitting performance of the VSD+ and DT models on neutral purple soil. (a) Observed (dots) and simulated (lines) changes in pH and (b) the scatter plot under six treatments by the VSD+ model; (c) observed and simulated changes in pH and (d) the scatter plot under six treatments by the DT model, respectively. CK, a control with no fertilizer; PK, mineral P and K, NPK, mineral N, P and K fertilizers; NPKS, mineral N, P and K plus straw; 1.5NPKS, 1.5 times mineral N, P and K plus straw; and NPKM, mineral N, P and K plus manure.



**Fig. S4** Comparison of the simulation and fitting performance of the VSD+ and SVM models on acidic purple soil. (a) Observed (dots) and simulated (lines) changes in pH and (b) the scatter plot under three treatments by the VSD+ model; (c) observed and simulated changes in pH and (d) the scatter plot under three treatments by the SVM model, respectively. CN, a control with non-N application but with optimized P and K; OP, optimal N, P and K application; and FP, farmer practice with excessive N, P and K application.



**Fig. S5** Comparison of the simulation and fitting performance of the VSD+ and XGB models on acidic purple soil. (a) Observed (dots) and simulated (lines) changes in pH and (b) the scatter plot under three treatments by the VSD+ model; (c) observed and simulated changes in pH and (d) the scatter plot under three treatments by the XGB model, respectively. CN, a control with non-N application but with optimized P and K; OP, optimal N, P and K application; and FP, farmer practice with excessive N, P and K application.



**Fig. S6** Comparison of the simulation and fitting performance of the VSD+ and DT models on acidic purple soil. (a) Observed (dots) and simulated (lines) changes in pH and (b) the scatter plot under three treatments by the VSD+ model; (c) observed and simulated changes in pH and (d) the scatter plot under three treatments by the DT model, respectively. CN, a control with non-N application but with optimized P and K; OP, optimal N, P and K application; and FP, farmer practice with excessive N, P and K application.

## REFERENCES

1. Posch M, Reinds G J. A very simple dynamic soil acidification model for scenario analyses and target load calculations. *Environmental Modelling & Software*, 2009, **24**(3): 329–340
2. Xu D H, Ros G H, Zhu Q C, Xu M G, Wen S L, Cai Z J, Zhang F S, de Vries W. Major drivers of soil acidification over 30 years differ in paddy and upland soils in China. *Science of the Total Environment*, 2024, **916**(3): 170189