

# **Supplementary Information**

## **Title Page**

### **Elevated Fe and Mn concentrations in groundwater in the Songnen Plain, Northeast China, and the factors and mechanisms involved**

Yuanzheng Zhai<sup>1</sup>, Xinyi Cao<sup>1</sup>, Xuelian Xia<sup>1</sup>, Bin Wang<sup>1</sup>, Yanguo Teng<sup>1,\*</sup>, Xiao Li<sup>2,\*</sup>

1 Engineering Research Center for Groundwater Pollution Control, Remediation of Ministry of Education of China, College of Water Sciences, Beijing Normal University, Beijing 100875, China

2 Shenyang Institute of Geology and Mineral Resources, CGS, Shenyang 110034, China

#### **Corresponding authors:**

1 Yanguo Teng at Beijing Normal University, Beijing 100875, China. E-mail: teng1974@163.com; phone: +86 010-58802738

2 Xiao Li at Shenyang Institute of Geology and Mineral Resources, CGS, Shenyang 110034, China. E-mail: ZZLX19@163.com; phone: +86 024-81847057

### **Table captions**

**Table S1.** Methods for determining water quality indicators and the corresponding detection limits.

**Table S2.** Data sources used in the study.

**Table S3.** Statistical data for the Fe and Mn concentrations in the groundwater samples.

**Table S4.** Summary of the Fe and Mn concentrations in the groundwater samples grouped by the influencing factors.

**Table S1.** Methods for determining water quality indicators and the corresponding detection limits.

Test indicator	Unit	Test site	Test method	Detection limit
pH	—	Portable multi-parameter rapid water quality analyzer Field		—
TDS		(HANNA-HI9828)		1
TH		EDTA titration method		1
K				0.07
Ca				0.03
Na				0.02
Mg		Inductively coupled plasma optical emission spectrometry		0.02
Fe				0.004
Mn				0.0005
As	mg/L			0.001
TP		Ammonium molybdate spectrophotometry		0.01
HCO <sub>3</sub> <sup>-</sup>		Neutralization titration method		5
COD <sub>Mn</sub>		Acidic permanganate method		0.5
Cl <sup>-</sup>				0.007
SO <sub>4</sub> <sup>2-</sup>				0.046
NH <sub>4</sub> <sup>+</sup>		Ion Chromatography		0.025
NO <sub>3</sub> <sup>-</sup>				0.016
NO <sub>2</sub> <sup>-</sup>				0.016

TDS: total dissolved solids; TH: total hardness (calculated as CaCO<sub>3</sub>); TP: total phosphorus.

**Table S2.** Data sources used in the study.

Variables	Data sources	Organization
Map of annual meteorological precipitation		Resource and
Map of average meteorological temperature	<a href="https://www.resdc.cn/Default.aspx">https://www.resdc.cn/Default.aspx</a>	Environment Science and
Map of soil types		Data Center
Map land use types		

**Table S3.** Statistical data for the Fe and Mn concentrations in the groundwater.

Number of samples		Number of samples with elevated Fe/Mn	Percentage of samples with elevated Fe/Mn					Standard Deviation
			Min (mg/L)	Median (mg/L)	Max (mg/L)	Mean (mg/L)		
Fe	1332	697	52.3%	<DL	0.340	48.930	1.873	4.71
Mn	1332	776	58.3%	<DL	0.1800	10.4600	0.4976	0.86

samples

DL: detection limit.

**Table S4.** Summary of the Fe and Mn concentrations in the groundwater samples grouped by the influencing factors.

Influencing factors		Fe (mg/L)						Mn (mg/L)						
		Number of samples	Number of samples with Fe>0.3	Percentage of samples with Fe>0.3			Number of samples	Number of samples with Mn>0.1	Percentage of samples with Mn>0.1			Min	Median	Max
				Min	Median	Max			Min	Median	Max			
Annual meteoric precipitation (mm)	(300,400]	99	39	39.4%	<DL	0.190	48.930	99	43	43.4%	<DL	0.0800	4.1300	
	(400,500]	516	284	55.0%	<DL	0.390	47.980	516	336	65.1%	<DL	0.2100	8.1130	
	(500,600]	678	349	51.5%	<DL	0.323	48.760	678	374	55.2%	<DL	0.1579	10.4600	
	(600,700]	39	25	64.1%	<DL	0.574	9.530	39	23	59.0%	<DL	0.2478	2.3990	
Annual average meteoric temperature (°C)	(1,3]	75	25	33.3%	<DL	0.117	18.540	75	29	38.7%	<DL	0.0410	1.9730	
Altitude (m)	(3,5]	304	149	49.0%	<DL	0.267	41.700	304	151	49.7%	<DL	0.0924	10.4600	
	(5,6]	471	280	59.4%	<DL	0.510	48.760	471	313	66.5%	<DL	0.3160	8.1130	
	(6,7]	482	243	50.4%	<DL	0.310	48.930	482	283	58.7%	<DL	0.1604	8.0150	
	(0,140]	250	201	80.4%	<DL	1.360	48.930	250	205	82.0%	<DL	0.3555	7.8400	
Distance to the nearest river (km)	(140,160]	414	231	55.8%	<DL	0.412	43.310	414	288	69.6%	<DL	0.2516	10.4600	
	(160,180]	224	103	46.0%	<DL	0.255	14.260	224	122	54.5%	<DL	0.1950	8.0150	
	(180,400]	444	162	36.5%	<DL	0.140	21.650	444	161	36.3%	<DL	0.0369	4.0400	
	(0,5]	252	149	59.1%	<DL	0.532	13.310	252	156	61.9%	<DL	0.2050	10.4600	
	(5,10]	199	116	58.3%	<DL	0.548	47.980	199	118	59.3%	<DL	0.2100	7.8400	
	(10,40]	533	293	55.0%	<DL	0.400	48.930	533	316	59.3%	<DL	0.2100	6.3880	
	(40,150]	348	139	39.9%	<DL	0.210	22.990	348	186	53.4%	<DL	0.1300	8.0150	

Influencing factors	Fe (mg/L)							Mn (mg/L)					
	Number of samples	Number of samples with Fe>0.3	Percentage of samples with Fe>0.3			Number of samples	Number of samples with Mn>0.1	Percentage of samples with Mn>0.1			Min	Median	Max
			Min	Median	Max			Min	Median	Max			
Soil type	Dark-brown earths	14	4	28.6%	<DL	0.120	1.902	14	6	42.9%	<DL	0.0670	1.0200
	Black soils	263	145	55.1%	<DL	0.408	48.760	263	153	58.2%	<DL	0.1833	10.4600
	Chernozems	343	172	50.1%	<DL	0.310	48.930	343	197	57.4%	<DL	0.1996	5.1730
	Castanozems	19	10	52.6%	<DL	0.315	7.257	19	11	57.9%	<DL	0.1500	0.4400
	Aeolian sandy soils	150	78	52.0%	<DL	0.326	32.840	150	95	63.3%	<DL	0.1800	8.0150
	Meadow soils	444	238	53.6%	<DL	0.374	43.310	444	256	57.7%	<DL	0.1846	8.1130
	Bog soils	24	13	54.2%	<DL	0.532	16.920	24	13	54.2%	<DL	0.1256	0.5617
	Solonchaks	11	5	45.5%	<DL	0.280	11.850	11	7	63.6%	<DL	0.2100	0.7700
	Solonetz	29	16	55.2%	<DL	0.460	14.280	29	20	69.0%	<DL	0.1700	3.4100
	Paddy soils	15	5	33.3%	<DL	0.180	9.041	15	4	26.7%	<DL	0.0400	1.26400
Soil texture	Water body	16	9	56.3%	<DL	0.870	47.980	16	11	68.8%	<DL	0.2100	7.8400
	Sand	72	38	52.8%	0.01	0.325	16.490	72	46	63.9%	<DL	0.1800	8.0150
	Loam	407	189	46.4%	<DL	0.250	43.310	407	228	56.0%	<DL	0.1600	8.1130
	Clay	849	467	55.0%	<DL	0.410	48.930	849	500	58.9%	<DL	0.1960	10.460
Land use type	Paddy field	92	57	62.0%	<DL	0.646	43.310	92	57	62.0%	<DL	0.3139	8.1130
	Dryland	782	387	49.5%	<DL	0.2778	48.930	782	436	55.8%	<DL	0.1600	10.4600
	Forest land	37	17	45.9%	<DL	0.259	48.760	37	19	51.4%	<DL	0.1400	1.3310
	Grassland	113	52	46.0%	<DL	0.266	11.330	113	64	56.6%	<DL	0.1715	6.3880

		Fe (mg/L)						Mn (mg/L)						
Influencing factors		Number of samples	Number of samples with Fe>0.3	Percentage of samples with Fe>0.3			Number of samples	Number of samples with Mn>0.1	Percentage of samples with Mn>0.1			Min	Median	Max
				Min	Median	Max			Min	Median	Max			
	Water body	73	43	58.9%	<DL	0.6700	47.980	73	47	64.4%	<DL	0.2384	7.8400	
Land use type	Construction land	58	38	65.5%	<DL	0.455	18.160	58	35	60.3%	<DL	0.1500	2.6760	
	Unutilized land	175	102	58.3%	<DL	0.460	30.240	175	118	67.4%	<DL	0.2151	4.3990	
Groundwater type	Fissure water	73	43	58.9%	<DL	0.710	41.700	73	35	47.9%	<DL	0.3368	48.9300	
	Pore water	1156	603	52.2%	<DL	0.337	48.930	1156	671	58.0%	<DL	0.1000	3.438	
Depth of groundwater level	(0,5]	707	370	52.3%	<DL	0.340	47.980	707	400	56.6%	<DL	0.1710	10.4600	
	(5,10]	503	257	51.1%	<DL	0.320	48.930	503	302	60.0%	<DL	0.1900	8.1130	
COD <sub>Mn</sub>	(10,20]	99	63	63.6%	<DL	0.510	48.760	99	63	63.6%	<DL	0.2800	4.3310	
	≤1	475	156	32.8%	<DL	0.140	47.980	475	168	35.4%	<DL	0.0200	8.1130	
NH <sub>4</sub> <sup>+</sup>	1-2	467	265	56.7%	<DL	0.441	37.120	467	317	67.9%	<DL	0.2853	6.3880	
	>2	390	276	70.8%	<DL	0.893	48.930	390	291	74.6%	<DL	0.3000	10.4600	
NO <sub>3</sub> <sup>-</sup>	≤0.5	1082	472	43.6%	<DL	0.210	37.120	1082	542	50.1%	<DL	0.1011	10.4600	
	0.5-1	130	114	87.7%	<DL	2.185	48.930	130	124	95.4%	<DL	0.7450	6.3880	
	>1	118	111	94.1%	<DL	3.222	48.760	118	110	93.2%	<DL	0.4750	8.1130	
	≤1	393	302	76.8%	<DL	1.471	48.760	393	321	81.7%	<DL	0.4500	8.1130	
	1-10	351	227	64.7%	<DL	0.576	48.930	351	255	72.6%	<DL	0.2900	7.8400	
	10-50	213	68	31.9%	<DL	0.126	21.650	213	90	42.3%	<DL	0.0500	6.3880	
	>50	375	100	26.7%	<DL	0.120	18.540	375	110	29.3%	<DL	0.0268	10.4600	

Influencing factors	Fe (mg/L)							Mn (mg/L)					
	Number of samples	Number of samples with Fe>0.3	Percentage of samples with Fe>0.3			Number of samples	Number of samples with Mn>0.1	Percentage of samples with Mn>0.1			Min	Median	Max
			Min	Median	Max			Min	Median	Max			
Total phosphorus	≤0.02	163	39	23.9%	<DL	0.086	32.840	163	64	39.3%	<DL	0.0351	10.4600
	0.02-0.1	202	74	36.6%	<DL	0.137	36.020	202	73	36.1%	<DL	0.0528	3.4930
	0.1-0.4	190	126	66.3%	<DL	0.637	48.760	190	129	67.9%	<DL	0.2228	8.1130
	>0.4	174	157	90.2%	<DL	3.062	41.700	174	155	89.1%	0.0086	0.7345	4.3990

DL: detection limit.

## **Figure captions**

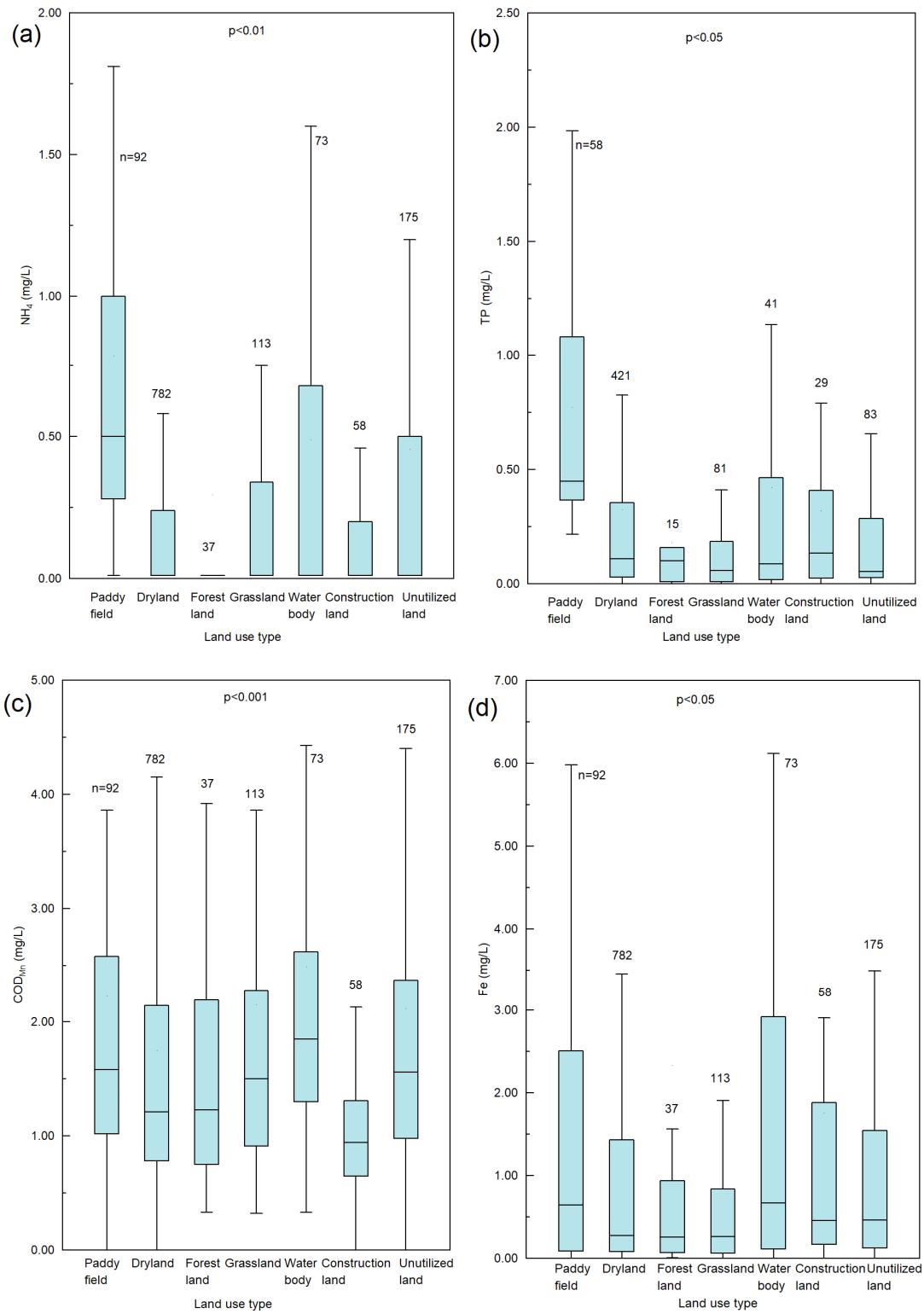
**Figure S1.**  $\text{NH}_4^+$  concentrations, total phosphorus (TP) concentrations, and chemical oxygen demand ( $\text{COD}_{\text{Mn}}$ ) compared with the Fe and Mn concentrations in groundwater in areas with different land use types.

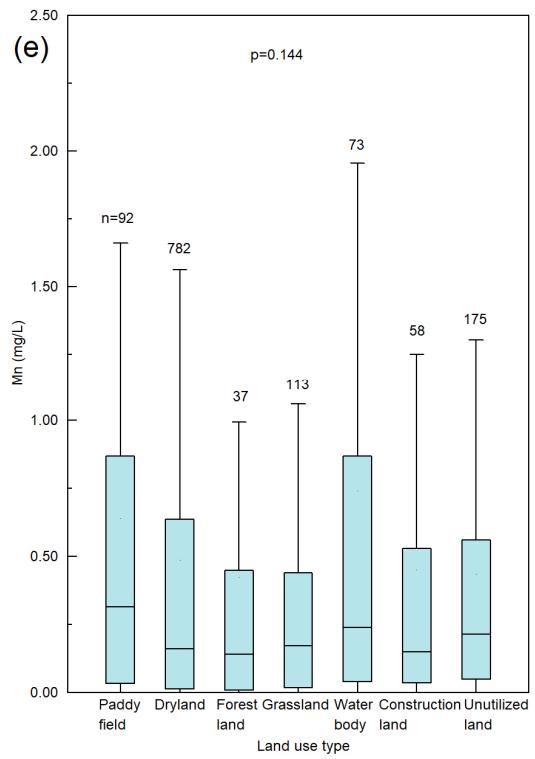
**Figure S2.** Overlay of the sampling points with high  $\text{NH}_4^+$  concentrations, total phosphorus (TP) concentrations, and chemical oxygen demand ( $\text{COD}_{\text{Mn}}$ ) in groundwater on a land use map.

**Figure S3.** Overlay of the sampling points with high  $\text{NH}_4^+$  concentrations, total phosphorus (TP) concentrations, and chemical oxygen demand ( $\text{COD}_{\text{Mn}}$ ) in groundwater on a map of the distributions of the Fe and Mn concentrations in groundwater.

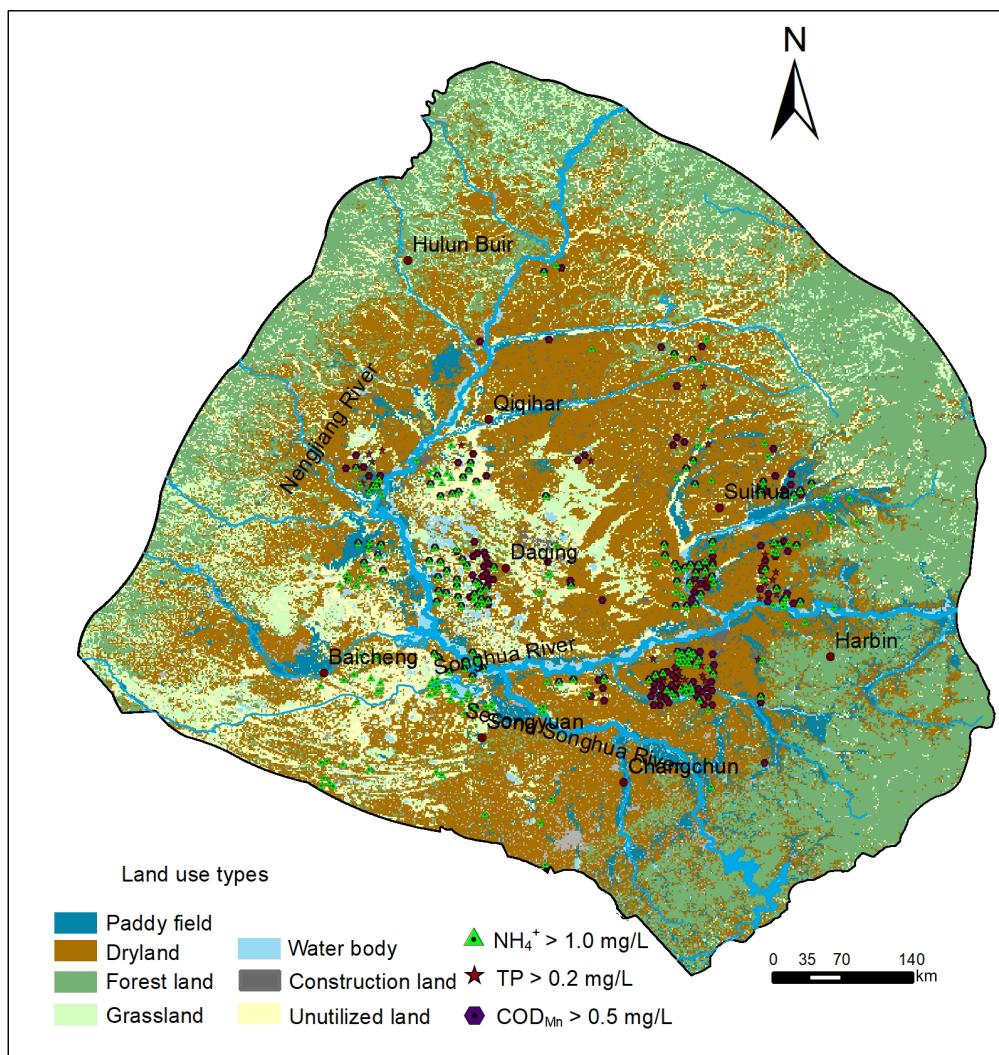
**Figure S4.** Annual meteorological precipitation in 2015 in the study area.

**Figure S5.** Annual average meteorological temperature in 2015 in the study area.

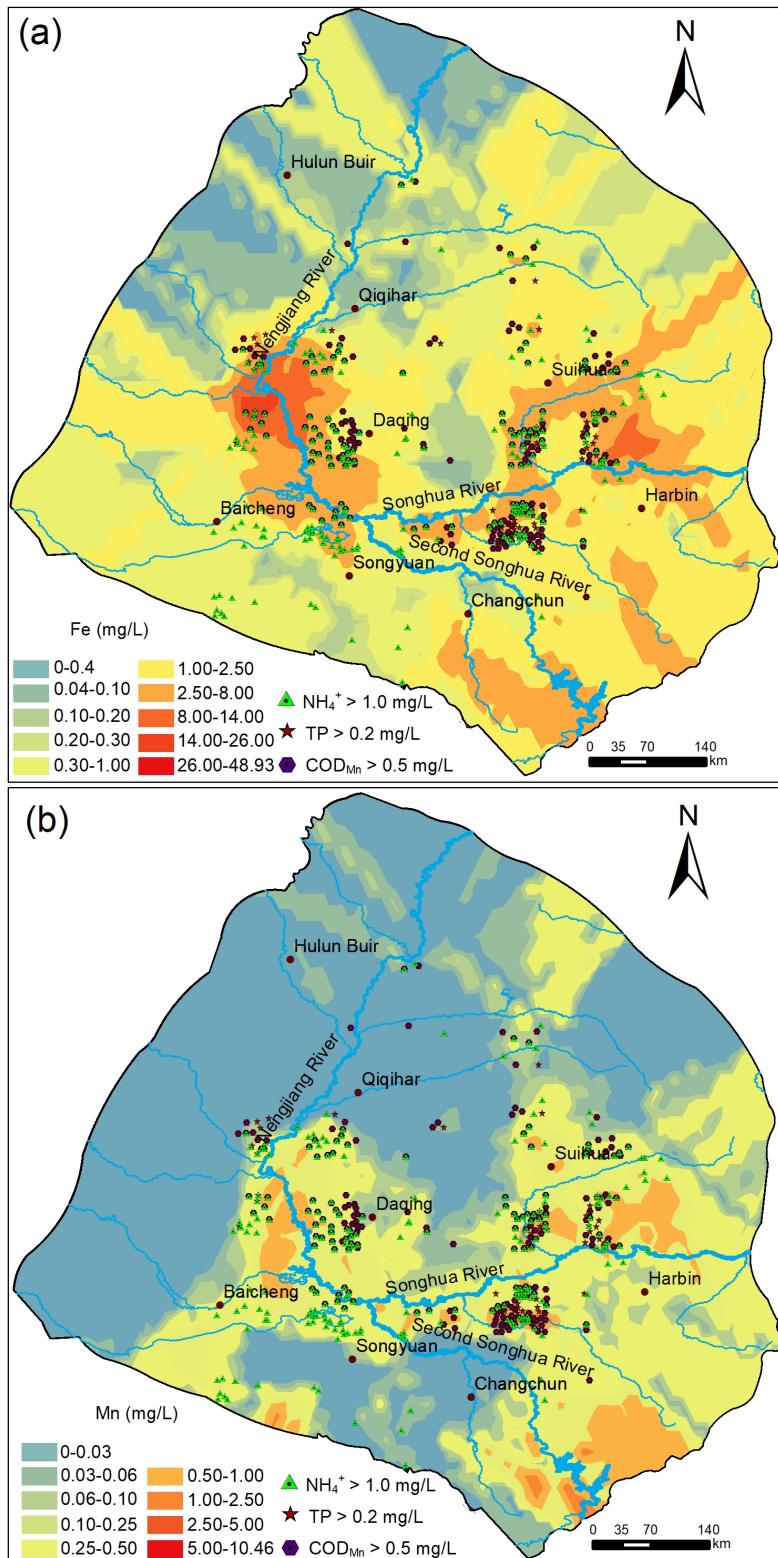




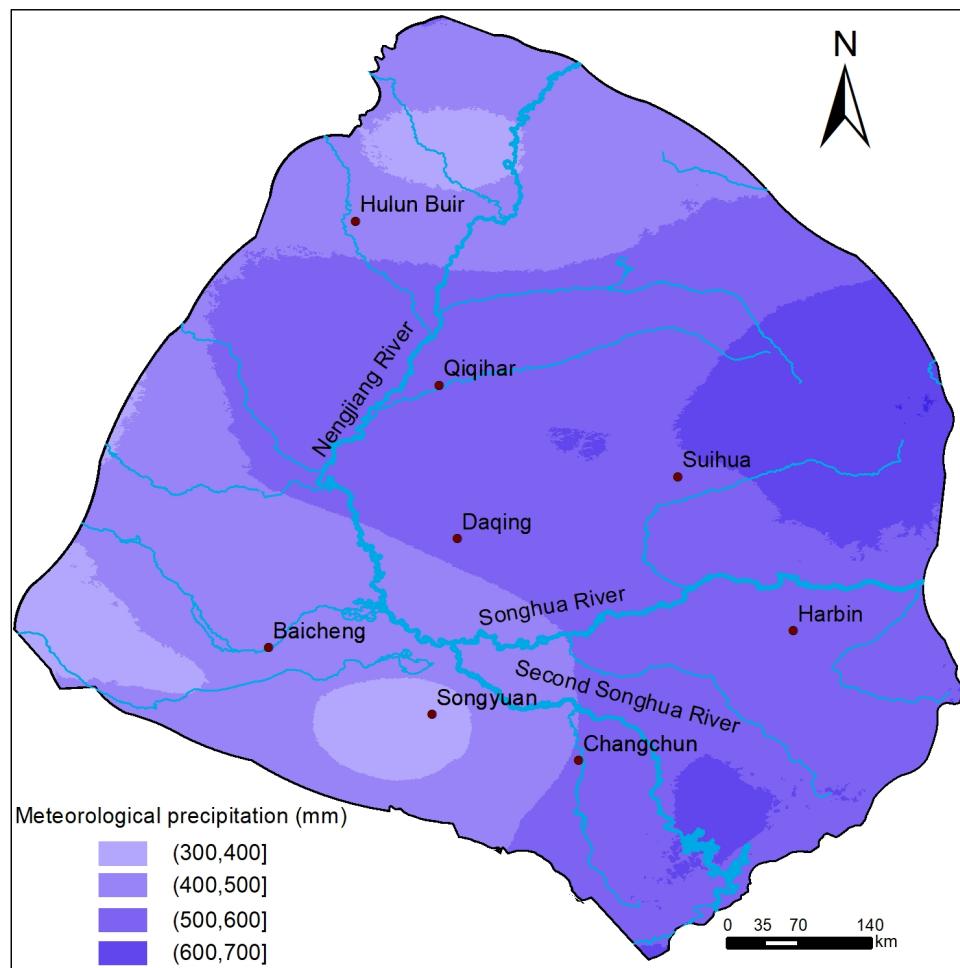
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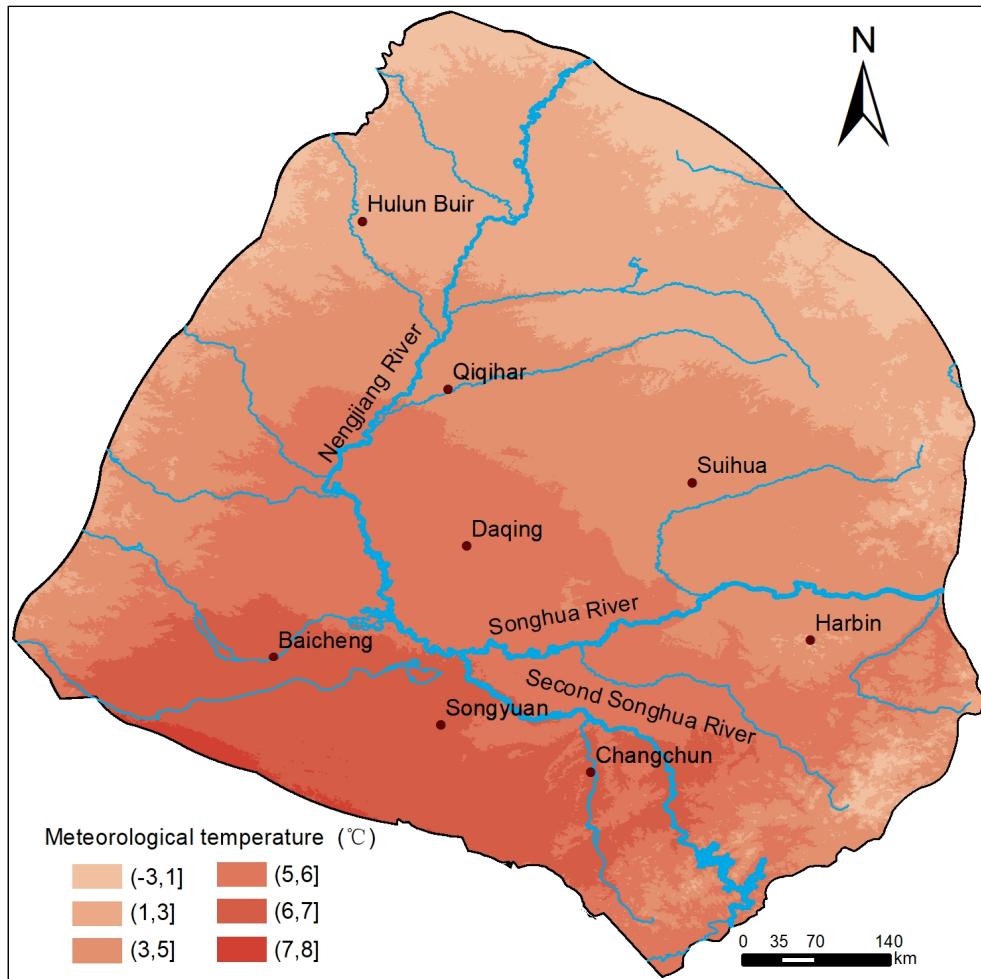
**Figure S2.** Overlay of the sampling points with high  $\text{NH}_4^+$  concentrations, total phosphorus (TP) concentrations, and chemical oxygen demand ( $\text{COD}_{\text{Mn}}$ ) in groundwater on a land use map.



**Figure S3.** Overlay of the sampling points with high  $\text{NH}_4^+$  concentrations, total phosphorus (TP) concentrations, and chemical oxygen demand ( $\text{COD}_{\text{Mn}}$ ) in groundwater on a map of the distributions of the Fe and Mn concentrations in groundwater.



**Figure S4.** Annual meteorological precipitation in 2015 in the study area.



**Figure S5.** Annual average meteorological temperature in 2015 in the study area.