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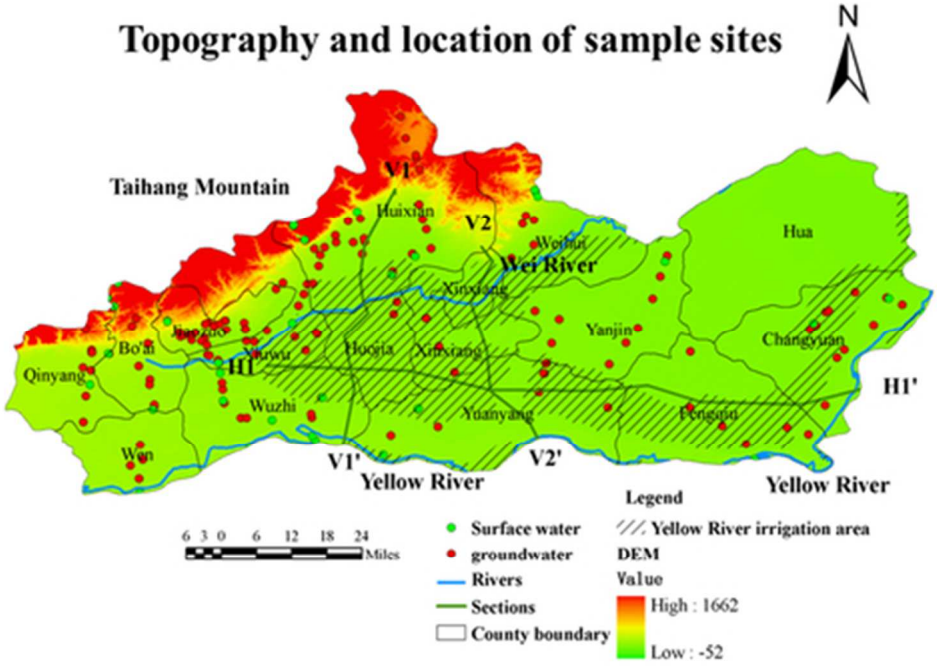

The Yellow River irrigation practice was a critical factor impacting the spatial distribution of nitrate in surface water and groundwater in a Yellow River alluvial fan.
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Nitrogen pollution is a burning topic in water management and often closely related to irrigation and fertilization in agriculture. The pollution and transfer migration mechanisms of nitrate (NO_3^-) in surface water and groundwater as related to irrigation practices were investigated in the catchment of the Yellow River North China. Substantial efforts in collecting some valuable data sets (include hydrochemical and isotopic data) and assessing the best out of them were made. Understanding the dynamics of NO_3^- contamination is critical to identify the sources and to explain the occurrence, fate and distribution of NO_3^- in waters.

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ARTICLE

Nitrate pollution and its transfer in surface- and ground-waters in irrigated areas: A case study of the Piedmont of South Taihang Mountains, China

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Irrigation projects have diverted water from the lower reaches of Yellow River for more than 50 years in China and are unique in the world. This study investigated the effect of irrigation practices on the transfer and regional migration mechanisms of nitrate (NO_3^-) in surface water and groundwater in a Yellow River alluvial fan. Hydrochemical indices (EC, pH, Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}, and HCO_3^-) and stable isotopic composition ($\delta^{18}O$ and δD) were determined for samples. Correlation analysis and Principal component analysis (PCA) were performed to identify the sources of water constituents. Kriging were employed to simulate the spatial diffusion of NO_3^- and stable isotopes. Our results demonstrated that, the groundwater exhibited more complex saline conditions than the surface water, likely resulting from alkaline conditions and lixiviation. NO_3^- was detected in all samples, 87.0% of which were influenced by anthropogenic activity. The NO_3^- pollution in groundwater was more serious than the common groundwater irrigation areas in North China Plain (NCP), and was also slightly higher than that in surface water in the study area, but was not statistically significant (P >0.05). Additionally, the groundwater sites with higher NO_3^- concentrations did not overlap with the spatial distribution of fertilizer consumption, especially in the central and western parts of the study area. NO_3^- distributions along the hydrogeological cross-sections were related to the groundwater flow system. Hydrochemical and environmental isotopic evidences indicate that surface - groundwater interactions influence the spatial distribution of NO_3^- in the Piedmont of South Taihang Mountains.

1. Introduction

Water resources commonly suffer from nitrate contamination,[1] especially in irrigated agricultural fields.[2, 3] High nitrate (NO_3^-) concentration in drinking water increases human health risks. Also, nitrate can transfer between surface- and ground- water, especially after fertilization and irrigation in agricultural regions.[4] The issue of the influence of irrigation practices on surface and groundwater contamination by nitrate is of great significance and interest to the international scientific community. According to several hydrology studies,[5, 6] the large-scale irrigation project might have a distinct influence on the regional hydrological cycle and water/nitrogen migration in the North China Plain (NCP). Recently, researchers have assessed and forecasted the regional water quantities in the Yellow River irrigation areas.[7, 8] However, data related to the impact of nitrogen transfer resulting from irrigation projects and the regional migration direction and flux in surface water and groundwater are limited.

The lower reaches of Yellow River irrigation area refers to the area from Peach Blossom Valley to the estuary of Yellow River.[9] The total area of the lower reaches of Yellow River irrigation area is 22.22 million ha, accounting for 51.4% of the total irrigation area of the Yellow River basin. Total available water resources in this region are 12.54 billion m^3, accounting for 33.9% of total water

resources of the Yellow River basin.[9] Because the seasonal distribution and volume of precipitation do not satisfy crop requirements, irrigation water has become an essential resource for agricultural production.[10] Percent irrigated areas have reached more than 80% and grain yields amount to 11250-15000 kg/ha (annual double cropping). However, long-term irrigation by the Yellow River water diversion project, low water and fertilizer use efficiency introduce a variety of environmental concerns.[11, 12] In addition, many rivers that provide water for irrigation are known to be contaminated.[13] In China, wastewater from industries and cities was used for irrigation as early as the 1940s. Wastewater-irrigated land increased from 1.17×10^4 ha in 1957 to 1.39×10^6 ha in 1982.[14]

NO_3^- is a major water pollutant and one of the key nutrients causing eutrophication of fresh and marine waters in China and the whole world.[12, 13] Additionally, NO_3^- is a very common constituent in the ground water, especially in shallow aquifers.[15] NO_3^- can originate from various anthropogenic sources, such as fertilizers, animal manure, domestic waste water, septic tanks, as well as organic nitrogen from soil.[1] NO_3^- in groundwater usually derives from non-point sources (chemical fertilizers) and point sources (septic tanks, sewage system, and animal/human manures).[16]

Previous and on-going investigations have demonstrated that the surface water in one part of the Yellow River irrigation area, the Dezhou irrigation area, was subject to NO_3^- pollution, with groundwater more affected than surface water.[17] Because of the decrease in salinity of the shallow groundwater resulting from long-term irrigation practices, groundwater has gradually replaced surface water as drinking water in rural areas, although the NO_3^- pollution of both surface water and groundwater exists commonly in the region. High ingestion of NO_3^- may cause hypertension,[18] increase infant mortality,[19] central nervous system birth defects,[20] and cause certain cancers and non-Hodgkin's lymphoma.[15] Given these concerns, it is imperative to evaluate the sources of nitrate pollution and its migration behavior from surface water to groundwater, or other means of inter-transfer in the Yellow River irrigation area. Samples (33 surface water, 157 groundwater and 13 rainfall samples) were collected during a field survey in order to: (1) identify the hydrochemical characteristics and quantify the NO_3^- content in the surface water and groundwater of the Piedmont of South Taihang Mountains; (2) reveal the spatial distribution of NO_3^-; (3) analyze the factors that influence the spatial distribution of NO_3^-; and (4) assess the effects of long-term Yellow River irrigation practices on NO_3^- pollution. The results of this study are important for evaluating water quality and promoting sustainable water management in irrigation regions.

2. Materials and Methods

2.1. Study area

The Yellow River Irrigation area of southern Taihang Piedmont region (113°00′-116°10′ E, and 34°50′-36°20 N) is a part of the NCP, located in the north of Henan province, adjacent to Hebei province in the North, and close to Shanxi province in the West (Fig.1). The total area is approximately 2.0×10^4 km^2 and includes five cities (i.e., Anyang, Xinxiang, Hebi, Jiaozuo, and Jiyuan), and is inhabited by 14.3 million people. The study area has a temperate climate with an average annual air temperature of about 13.6°C, and a maximum and minimum monthly temperature of 26.3°C and -1.6°C in July and January, respectively. Annual precipitation ranges from 600 to 1000 mm, with most of it falling between June and September. Rivers include the Yellow River, the Wei River, and their main tributaries. The abundant water resource promoted this area as a major region for agriculture development and has been the production base of wheat, rice, and corn in North China. In 2006, the total amount of food production of Anyang, Xinxiang, Hebi, Jiyuan, and Jiaozuo reached 10.02 million tons, representing 20% of food production in Henan province and 3% of the national grain output.[21, 22]

2.2. Water sampling

Thirty-three surface water samples and 157 groundwater samples were collected during the irrigation period from July to September in 2007 (Fig.1). Surface water samples were taken from the Yellow River, its main tributaries, old channels, irrigation ditches, reservoirs, and around cities, towns and branch afflux sites (Supplementary Table A). Groundwater samples were collected from private, factory, and observation wells of locations in the study area. All samples were collected using high-density polyethylene (HDPE) bottles for isotopic analyses. Thirteen rainfall samples were collected for isotope analysis after storm events (Supplementary Table B). A general overview of the study site showing the topography and the sampling locations is presented in Fig.1.

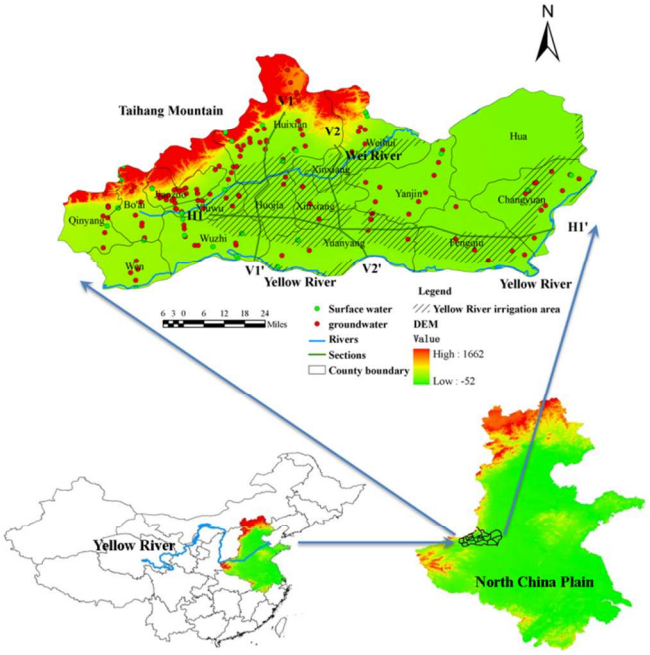

Fig.1 Topography and location of sample sites

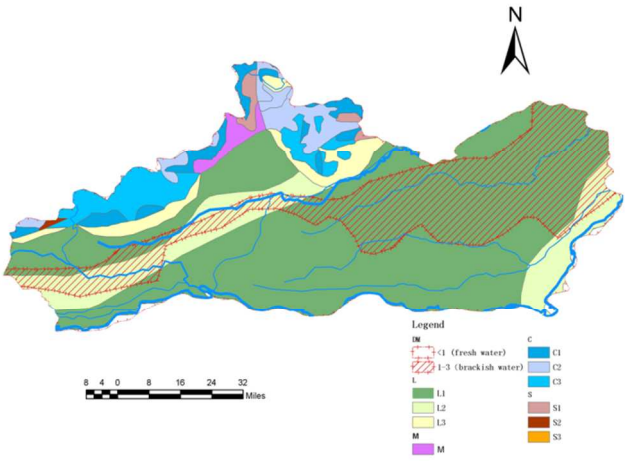

Fig.2 Hydrogeological settings of the study area

(Note: "L," loose salts porous aquiferous group (water-rich intensity gradually increasing from L1 to L3); "M," metamorphic rocks fractured aquifer rock group; "C," carbonate fissure salt dissolved water content of salt groups (water-rich intensity gradually increasing from C1 to C3); "S," broken nitrate aquiferous group (water-rich intensity gradually increasing from S1 to S3)).

2.3. Hydrogeological settings

The Piedmont of the South Taihang Mountains is the transitional region of terrain ladders II and III in China, rendering high terrains in the west to low terrains in the east, and consists of mountains, hills, basins and plains. A hydrogeological map of the area is shown in Fig. 2. The strata of the North Henan Plain were deposited during the Archean to the Cenozoic time periods, and subsequently, during the Quaternary, alluvium was widely distributed in the North Henan Plain.[23] The alluvium thickness in the Piedmont area is less than 100 m; it increases to more than 180 m toward the plain and in some areas reaches thicknesses of more than 400 m. Pore water in Quaternary unconsolidated rock is the main type of groundwater in the plain.[24] The shallow groundwater table has declined at a mean rate of approximately 1 m/year in this area over the past several decades, and the area of the groundwater cone of depression has expanded in Xinxiang in the NCP.[25] From 1974 to 2005, the water table in Xinxiang decreased from 6 m to 18 m, and exhibited severe groundwater pollution.[26]

2.4. Experimental analysis

Electrical conductivity (EC) and pH were measured by portable pH and EC meters (Compact meter, Horiba, Japan) on site. All samples were filtered through a 0.45 μm cellulose acetate filter membrane before using ion chromatography (Shimadzu, Japan) to analyze Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, and SO_4^{2-}. HCO_3^- was measured by titration using 0.01N H_2SO_4. The chemical results were only accepted when the charge balance error was within ±5%.

The stable isotopic compositions of oxygen (^{18}O) and deuterium (D) in groundwater and surface water were examined by an Isotope Ratio Mass Spectrometer (LGR LWIA-V2(DLT-100)) at Institute of Geographic Sciences and Natural Resources Research laboratories, Chinese Academic of Science. The results are expressed in units of per mil, using the delta-notation (δ) relative to Vienna Standard Mean Ocean Water (VSMOW) standard (Equation 1). The $\delta^{18}O$ and δD measurements were reproducible to ±0.3‰ and ±1.0‰, respectively.

$$\delta = \left(\frac{R_{sample}}{R_{stamdard}} - 1 \right) \times 1000 \qquad (1)$$

Where, R_{sample} and $R_{standard}$ are the measured isotopic ratio for sample and for standard, respectively.

2.5. Statistical analyses

Frequency distributions of concentrations of hydrochemical indexes, stable isotopes, and NO_3^- were investigated by calculating skewness and kurtosis coefficients. The difference of the NO_3^- pollution between surface water and groundwater was analyzed by analysis of variance (ANOVA). Correlation analysis and principal component analysis (PCA) were performed to identify the sources of hydrochemical ions in terms of the correlation coefficients among elements in water samples. Samples were grouped using varimax rotation and the identification of principal components (PC) that exhibited eigenvalues >1. Variables with similar characteristics were grouped into factors. IDW and Ordinary Kriging were employed to analyze the horizontal distribution of NO_3^- and stable isotopes, and spatial maps were generated by use of Arc GIS software version 9.0 for Windows (Esri China (Beijing) Limited).

3. Results and Discussion

3.1. Hydrochemical and stable isotopes characteristics

EC values in groundwater ranged from 222 μS/cm (W136) to 7040 μS/cm (W31) (Table 1). The mean values of EC in groundwater and surface water were 1071.12 ± 742.00 μS/cm and 728.77 ± 324.74 μS/cm, respectively. Low EC values in surface water were found in the Yellow River surface water, whereas the groundwaters had higher EC because of lixiviation from soil or from the mixing of different sources groundwater. All surface water samples were relatively similar in pH (6.84 - 8.26), while those of groundwater samples ranged from 6.69 to 8.39, indicating alkaline conditions.

Table 1 also shows the order of relative abundance of major cations in the studied waters ($Ca^{2+} > Na^+ > Mg^{2+} > K^+$ mg/L), and that of anions ($HCO_3^- > SO_4^{2-} > Cl^- > NO_3^-$). Ca^{2+} and HCO_3^- were the most abundant cation and anion in both ground and surface waters, and also several water samples contained high Na^+, Mg^{2+}, SO_4^{2-} and Cl^- concentrations. A piper diagram revealed that the surface waters comprised Ca-HCO_3, Ca•Na-HCO_3, Ca-HCO_3•SO_4, Ca-HCO_3•Cl, Mg•Ca-SO_4•HCO_3, and Ca•Na-SO_4 facies. The groundwater exhibited a more complex saline composition than the surface water.

Correlation analysis and PCA were used to identify the sources of elements, in terms of the correlation coefficients among elements, and to compare patterns of relative concentrations of ions in groundwater samples.[4, 27] Three PCs with eigenvalues >1 originated, accounting for 84.3% of the variance in the dataset (Fig. 3). The first PC accounted for 34.7% of the total variance and has high loadings of Na^+, K^+, Mg^{2+}, and SO_4^{2-}, which is indicative of geogenic origins and anthropogenic inputs. Na^+ was correlated with K^+ (R=0.52, P<0.01) and SO_4^{2-} (R=0.75, P<0.01) (Table 2). The background salt composition in the study area, controlled primarily by sediment mineralogy, was Na-SO_4.[28] The high K^+ concentration in the groundwater samples of the paddy fields, during the cultivation period, and the vegetables fields can be attributed to the use of chemical fertilizers. Sources of SO_4^{2-} include rainfall, chemical fertilizers ($(NH_4)_2SO_4$), manure, and the dissolution of sulfide minerals present in lacustrine sediments. The second PC accounted for 29.2% of the total variance and exhibits positive loadings of Ca^{2+} and Cl^- (R=0.56, P<0.01). Ca^{2+} could have originated from fertilizer ($Ca(H_2PO_4)_2 \cdot H_2O$),[12] although part of this will originate from the dissolution of carbonate rocks. Cl^- can be derived from pollution sources, including domestic wastewater, septic effluent, chemical fertilizers, and manure.[3] This component may be attributable to the fertilizer application. The third PC accounted for 20.4% of the total variance and is mostly influenced by HCO_3^-. Natural processes, such as the dissolution of carbonate minerals and of atmosphere and soil CO_2 gases may be the mechanisms that supply HCO_3^- to groundwater.[29] The mechanism can be explained as follows:

$$CaCO_3 + CO_2 + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^- \quad (2)$$

$$CO_2 + H_2O \leftrightarrow H^+ + HCO_3^- \quad (3)$$

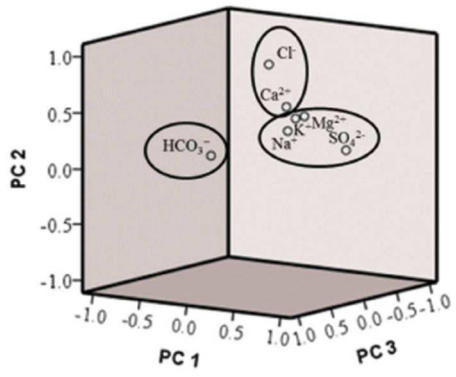

Fig.3 Total variance explained and component matrices of PCA

Table 1 Chemical constituents and stable isotopes in surface water and groundwater samples

Item	Groundwater								Surface water							
	N	Min.	Max.	Mean	Std	Kurtosis	Skewness	Coefficient of variation	N	Min.	Max.	Mean	Std	Kurtosis	Skewness	Coefficient of variation
Elevation(m)	157	55.00	560.00	124.59	96.22	8.61	2.99	4.05	33	62.00	618.00	169.30	161.10	2.85	1.97	3.28
EC(μS/cm)	157	222.00	7040.00	1093.38	752.54	25.18	3.88	6.24	33	360.00	1875.00	747.09	325.44	3.97	1.77	2.03
pH	157	7.16	8.26	7.63	0.20	0.55	0.36	0.14	33	6.96	8.39	7.82	0.29	2.96	-1.00	0.18
Na^+ (mg/L)	157	nd	598.51	61.74	80.65	15.08	3.38	9.69	33	nd	545.42	46.78	92.34	28.78	5.22	11.66
K^+ (mg/L)	157	nd	34.20	8.68	5.24	4.82	1.56	3.94	33	nd	17.37	6.62	3.55	3.17	1.52	2.63
Mg^{2+} (mg/L)	157	nd	491.67	62.18	58.09	19.97	3.53	7.91	33	nd	145.97	32.62	27.02	9.84	2.93	4.47
Ca^{2+} (mg/L)	157	nd	306.40	88.11	41.90	6.03	1.60	3.48	33	nd	230.97	76.47	37.96	8.35	2.20	3.02
Cl^- (mg/L)	157	nd	896.43	93.42	146.62	10.43	3.01	9.60	33	nd	450.33	58.24	86.78	13.30	3.41	7.73
NO_3^- (mg/L)	157	nd	440.87	42.22	50.24	27.31	4.26	10.44	33	1.69	69.34	33.69	19.56	-1.02	0.18	2.06
SO_4^{2-} (mg/L)	157	nd	2565.46	131.98	227.77	84.57	8.24	19.44	33	nd	1007.98	133.27	175.84	20.45	4.32	7.56
HCO_3^- (mg/L)	157	nd	954.65	385.68	165.26	0.39	0.53	2.48	33	nd	741.15	228.75	114.32	12.90	2.86	3.24
δD	157	-78.47	-51.88	-62.10	4.27	1.60	-0.65	0.43	33	-71.26	-35.14	-58.55	6.40	5.33	1.56	0.62
$\delta^{18}O$	157	-12.33	-5.40	-8.36	0.99	1.94	-0.31	0.83	33	-11.56	-4.30	-7.62	2.00	12.58	2.71	0.95

nd: not detected.

Table 2 Correlations among elements in groundwater samples

	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	HCO_3^-
Na^+	.52**	.78**	.47**	.68**	.75**	.66**
K^+		.78**	.79**	.64**	.65**	.41**
Mg^{2+}			.70**	.76**	.84**	.55**
Ca^{2+}				.70**	.59**	.43**
Cl^-					.48**	.47**
SO_4^{2-}						.27**

Notes: **Correlation is significant at the 0.01 level (2-tailed).

Stable isotopes ($\delta^{18}O$ and δD) can provide useful information on the sources of water. δD values in rainfall varied from -64 to -33‰ with mean value of -53‰, and $\delta^{18}O$ ranged from -11.2 to -4.5‰ with mean value of -7.7‰. δD values in groundwater varied from -78 (W25 in Hua county) to -52‰ (W103 in Hui county) with mean value of -62‰-, and $\delta^{18}O$ varied from -12.3 (W106 in Xinxiang county) to -5.4‰ (W194 in Jiaozuo county) with mean value of -8.4‰. δD values in surface water fluctuated from -71 (W32 in Xiuwu county) to -35‰ (W113 in Yuanyang county) with mean value of -59‰, and $\delta^{18}O$ differed from -11.6 (W153 in Hui county) to 1.3‰ (W113 in Yuanyang county) with mean value of -7.8‰.

3.2. Distribution and risk assessment of NO_3^- in the surface water and groundwater

NO_3^- was detected in 100% of surface water samples in the study area (Table 1**Error! Reference source not found.**), and concentrations varied from 1.69 mg/L to 69.34 mg/L, with a mean value of 32.51 mg/L. NO_3^- in groundwater was detected in 99.4% of groundwater samples, and concentrations ranged from below the limit of detection (not detected, nd) to 440.87 mg/L, with a mean value of 41.10 mg/L. Because of NO_3^- concentrations greater than approximately 10 to 15 mg/L (as NO_3^-) are generally indicative of anthropogenic NO_3^- sources,[30] 87.0% of water samples in the study area appeared to be influenced by the anthropogenic NO_3^-.[15]

The World Health Organization, Europe, and the United States Environmental Protection Agency regulate the Maximum Contaminant Level (MCL) for NO_3^- in drinking water, which ranges from 45 - 50 mg/L.[15] NO_3^- regulations in drinking water standards have been enacted since 1986 in China, level I was 45 mg/L; level II was 90 mg/L (equivalent to China national groundwater quality standard class III for human health protection).[31] By combining the international and Chinese drinking water criteria of NO_3^-, we generated four levels to evaluate the water quality (Table 3). According to the water quality standard proposed, only 5.9% of the surface water samples fall in level I (<13.5 mg/L),[15] 32.4% in level II (13.5-22.5 mg/L,), 29.4% in level III (22.5-45 mg/L,), and 32.4% in level IV (>45 mg/L,). When evaluated using surface water criteria, 13.7%, 29.2%, 23.6%, and 33.5% of the groundwater samples were classified as level I II, III, and IV, respectively. Although the NO_3^- concentration in groundwater was slightly higher than that in surface water, the result of ANOVA showed that the severity of pollution did not differ significantly (P >0.05) between groundwater and surface water. In the NCP, less than 15% of groundwater samples collected in irrigation areas exceeded the WHO drinking water standard.[14] Comparatively, 33.5% of groundwater samples collected in the study area exceeded the WHO drinking water standard, indicating that the study area was more polluted with NO_3^- than the common groundwater irrigation areas in NCP.

Table 3 Classification and evaluation of NO_3^- in sampling water

Level	Description	NO_3-N (mg/L)	NO_3^- (mg/L)	Surface water	Ground-water
I	Very good, background level	0-3	0-13.5	5.9%	13.7%
II	Good	3-5	13.5-22.5	32.4%	29.2%
III	Normal, unpolluted but in the critical condition	5-10	22.5-45	29.4%	23.6%
IV	Polluted	>10	>45	32.4%	33.5%

3.3. Factors influencing the spatial distribution of NO_3^-

Fertilizer application

IDW and Ordinary Kriging, geostatistical plotting techniques, were used to impute values for areas that were not sampled or where data was not available.[29] The frequency histograms of NO_3^- data in groundwater and log-transformed NO_3^- data in surface water produced the same general unimodal distribution, suggesting they were normally distributed. Because of surface waters' auto-correlation along the stream network, IDW and Ordinary kriging were employed for mapping the distribution of NO_3^- in surface water

and groundwater, respectively. The types of semi-variogram model are presented as solid curves, with the experimental values plotted as points, and their three key terms - a nugget (C_0), a sill ($C+ C_0$), and a range (A) are presented in Fig. 4. As shown in Table 1, the variation coefficient of NO_3^- in groundwater (10.44) was five times larger than that in surface water (2.06), indicating greater spatial variability of nitrate concentration than in groundwater. NO_3^- pollution of groundwater occurred in the western, northwestern and southeastern parts of study area, whilst NO_3^- polluted surface water was located in the southwestern part of study area. Following the water flow of Yellow River and its tributaries, the NO_3^- in surface water drifted with the streams and became slightly variable during irrigation periods.

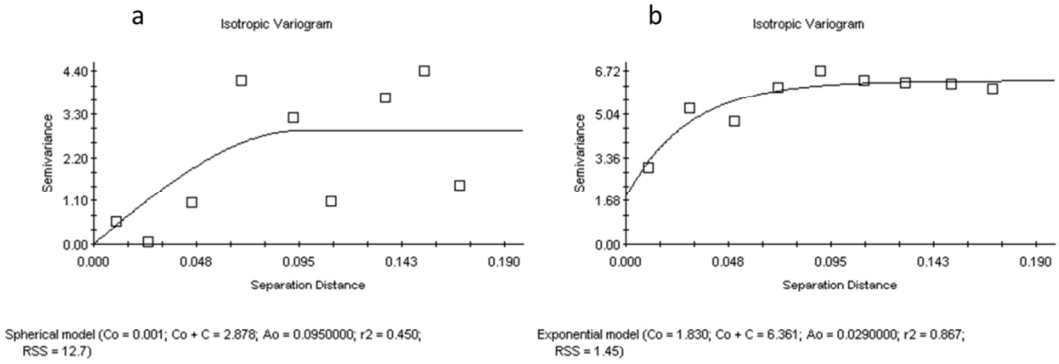

Fig. 4 Semivariograms of NO_3^- data in groundwater (a) and surface water (b) and key parameters

The factors influencing the spatial distribution of NO_3^- are diverse, including non-point sources (chemical fertilizers), point sources (waste water irrigation),[16] and migration impacted by the water cycling,[32] etc. The data for chemical fertilizer usage was collected from the Statistical Yearbook included in the Henan Rural Statistical Yearbook [22] and from China County Socio-Economic Statistical Yearbook.[21] In 2007, the total amount of fertilizer consumption in the study area was 12.05 million tons, the fertilizer intensity was 0.51 t/ha. The spatial distribution of fertilizer consumption, which exhibits a similar pattern as that of grain output (sum of winter wheat and summer corn), showed that the counties with the greatest fertilization were located in the southeast (Hua, and Huixian; Fig. 5). NO_3^- concentrations in groundwater are generally higher in areas with high nitrogen input, more well-drained soils, and low woodland to cropland ratio.[1] However, the sites that were more heavily polluted in groundwater NO_3^- were located in the west, northwest and southeast of the study area, including Qingyang, Bo'ai, part of Weihui and Fengqiu County. This pattern does not match the spatial distribution of fertilizer consumption, especially in the central and western areas of the study area. Fertilizer application was the main process that led to the cropland being the leading contributor to groundwater nitrate pollution.[3] There is about 5-10% of applied fertilizer that would enter into groundwater.[33] Many studies in the literature reported stronger correlations between 'groundwater nitrate contamination' and 'fertilizer application/croplands'.[34-36] However, different geological landforms (piedmont, low plain and coast plain), groundwater depth, water management and agricultural farming systems impacted the nitrate accumulation in the soil and surface water and lixiviation to groundwater bodies, nitrate concentration in groundwater showed regional differences in the study area.[33, 37]

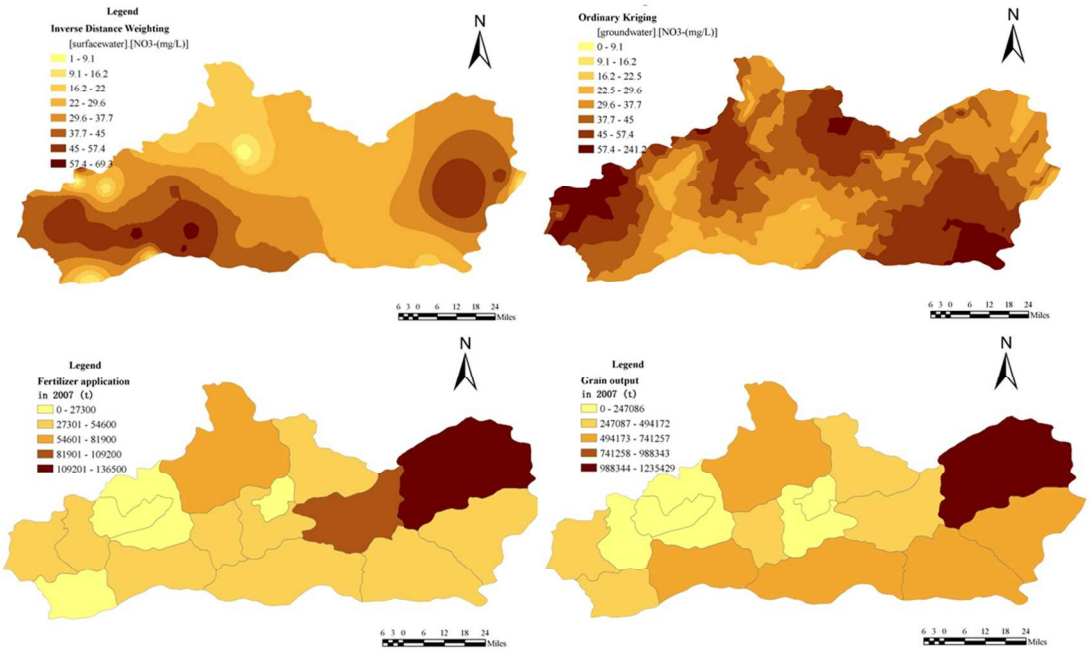

Fig.5 Spatial differences between fertilizer application and distribution of NO_3^- in surface water and groundwater

Surface - groundwater interactions influenced by irrigation

Chen et al.[32] found that the spatial distribution of NO_3^- in groundwater was closely related to the groundwater flow system in the NCP. The impact of the Yellow River on NO_3^- pollution in groundwater was examined further by the relationship between NO_3^- concentration and perpendicular distance to the Yellow River (Fig. 6). One hydrogeological cross-section along the direction of Yellow River flow (H1-H1') and two different cross-section perpendicular to the flow direction of Yellow River (V1-V1' and V2-V2') were selected to depict the evolvement of NO_3^- between the surface water and groundwater in the study area. In general, NO_3^- concentrations were higher downriver; similarly, the NO_3^- concentration of groundwaters increased along the H1- H1' cross-section. The concentration of NO_3^- in the Yellow River was relatively low compared to that in groundwater. NO_3^- concentration values in Yellow River varied from 8.33 mg/L to 38.57 mg/L, with mean value of 23.07 mg/L. Due to the low concentration of NO_3^- in Yellow River, the NO_3^- concentration in groundwater cross-section of Yellow River V1-V1' showed lower values closer to the river. However, the NO_3^- concentration in groundwater along the hydrogeological profiles V2-V2' did not exhibit a change across the cross-section. This cross-section may have been impacted by local anthropogenic activities and groundwater deposition.

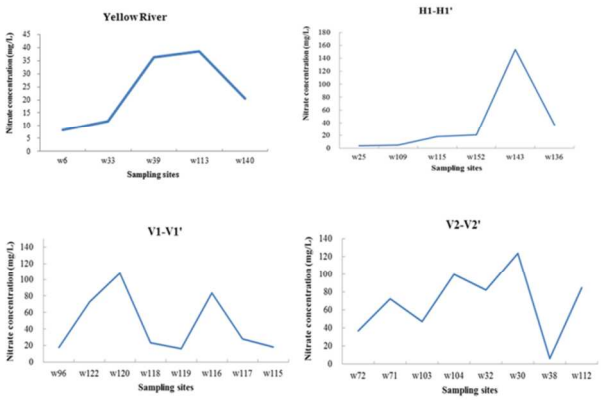

Fig.6 Fluctuation in NO_3^- concentration along the route of Yellow River and hydrogeological profiles

(Note: The order of the sampling sites in plot of Yellow River was along the direction of water flow, likewise in the plot of H1-H1'. The order of the sampling sites in plots V1-V1' and V2-V2' were from far to near the river, perpendicular to the direction of flow.)

Hydrochemical evidence of surface - groundwater interactions

Shallow groundwater freshening was observed in the groundwater, probably due to surface water infiltration, which influences hydrochemistry. The background salt composition of groundwater of the study area was Na-SO_4, which was controlled by sediment mineralogy of quaternary loose

sediment.[28] From 1960 to 2000, the Yellow River has displayed only minor variability in water chemistry and the dominant salt present is Ca-HCO_3.[38] The groundwater level has fallen in the exploited areas in the Piedmont of South Taihang Mountains. The dominant anions in most shallow groundwaters along the hydrogeological cross-sections are now HCO_3 and SO_4, whilst the dominant cationic structure are now Ca·Na, Na·Ca, Ca·Mg, Ca, and Mg·Ca (Fig. 7). The massive extraction of groundwater and Yellow River irrigation supply to the zone, thus alter the water cycle and the main ions in the shallow groundwater.[11] Hence, it appears that the Yellow River water provides, to some extent, a source of shallow groundwater recharge to the alluvial aquifer, especially during periods of rain and crop growth (from March to June).[28]

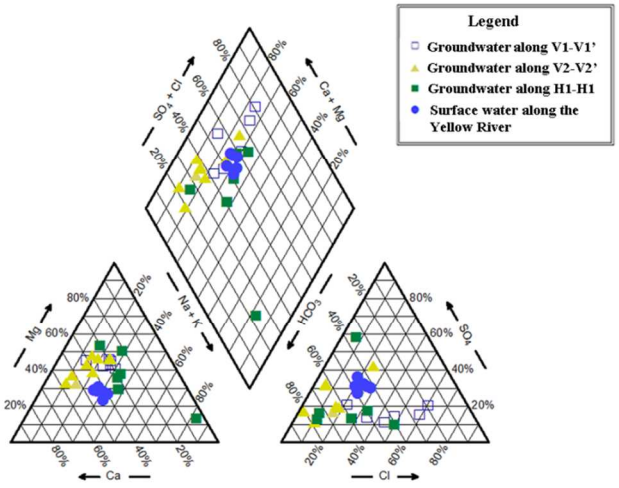

Fig.7 Piper diagram of surface water and groundwater samples along the flow of Yellow River and hydrogeological profiles

Isotopic evidence of surface - groundwater interactions

The relationship between $\delta^{18}O$ and δD composition of meteoric waters varied in a range that was close to the global meteoric water line (GMWL), defined as $\delta D=8\delta^{18}O+10$.[39] The relationship between $\delta^{18}O$ and δD composition of rainfall is different from one region to another and is dependent on local climatic conditions.[40] $\delta^{18}O$ and δD of rainfall data cited from the Global Network for Isotopes [41] were used to determine the Local Meteoric Water Line (LMWL, $\delta D=6.75\delta^{18}O-3$) shown in Fig.8. LMWL data were calculated according to monthly accumulated rainfall in Zhengzhou City from September 1985 to December 1992.[28] Fig.8 illustrates that some isotopic data points fell close to the GMWL and most of the points fell below the GMWL, suggesting effects of evaporation in different areas. The observed relationship between $\delta^{18}O$ and δD of the Yellow River water was as follows:

$$\delta D = 3.09\,\delta^{18}O - 38.94 \qquad R^2=0.98$$

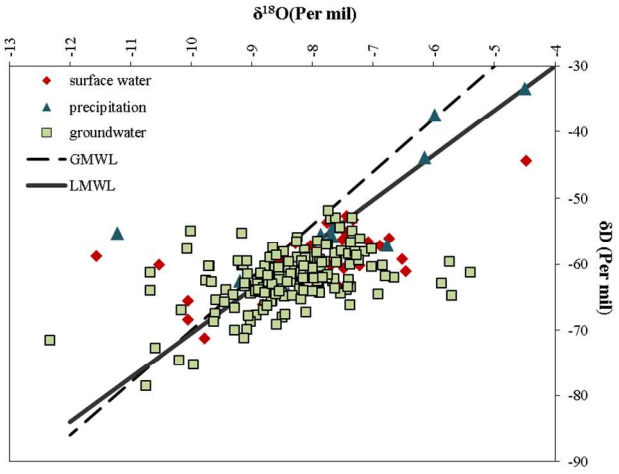

Fig.8 Plot of relationship of $\delta^{18}O$ and δD in the study area
(GMWL: the global meteoric water line, defined as $\delta D=8\delta^{18}O+10$.[39] LMWL: the Local Meteoric Water Line, $\delta^{18}O$ and δD of rainfall data cited from the Global Network for Isotopes, defined as $\delta D=6.75\delta^{18}O-3$.[41])

The Yellow River's tributaries are mainly concentrated in the upper and mid reaches of the river; there is less water supply from other rivers in the downstream region.[10] These areas also experience strong evaporation, and the ensuing isotopic fractionation results in enrichment along the Yellow River (Fig. 9). The root-mean-square of prediction error for $\delta^{18}O$ was 1.062 and 1.05 in surface water and groundwater, respectively, which is acceptable according to Oliver and Webster.[42] The majority of surface waters from the Yellow River fell below the LMWL and the slope of a linear equation of $\delta^{18}O$ and δD decreased to 3.58, reflecting the apparent evaporation characteristics that differ from the precipitation lines.

The ratio of $\delta^{18}O$ and δD compositions in groundwater plotted mostly along the LMWL. However, the groundwater isotopic compositions of $\delta^{18}O$ and δD exhibited a scattered and dispersed distribution (Fig. 8). Most of the groundwater sampling sites were distributed on both sides of GMWL and close to the rainfall line. The ranges of $\delta^{18}O$ and δD in groundwater were larger than in surface water, which indicated that the space of shallow groundwater was relatively open and the groundwater reservoir was affected by

seepage along the Yellow River, and thus infiltrated by chemical signatures of atmospheric precipitation.[28]

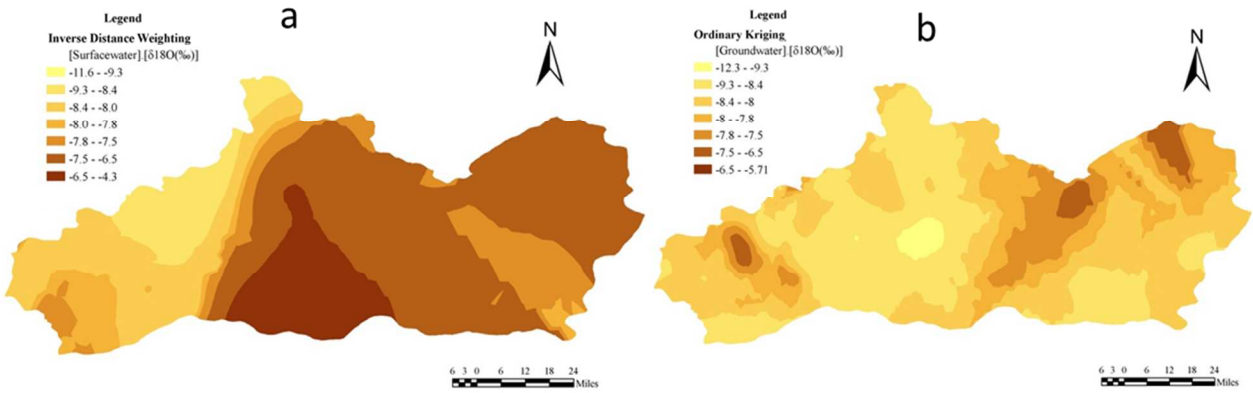

Fig.9 Spatial distribution of stable isotopes $\delta^{18}O$ in surface water and groundwater

Further analysis of the stable isotopes characteristics along the hydrogeological profiles exhibited the same relationship between $\delta^{18}O$ and δD (Fig. 10). Surface - groundwater interactions were identifiable by the $\delta^{18}O$ and δD values. Most points were distributed along or near the LMWL. Precipitation was thus a main source of surface water in the Yellow River alluvial fan.[9] The isotopic composition of groundwater samples along the Yellow River (H1) were similar to the surface water reservoir, indicating that the groundwater sources were affected by seepage from the perched riverbed of Yellow River and infiltration of irrigation waters during the growing season of winter wheat, a crop grown throughout the study area. The low $\delta^{18}O$ and δD values of groundwater samples along horizontal and perpendicular cross sections of the Yellow River indicate that the groundwater reservoir is mainly recharged by the seepage of Yellow River water, as seen by the slope of the regression curve for the horizontal (H1-H1') and perpendicular cross-sections (V1-V1', and V2-V2'), with values of 4.72, 3.49, and 3.58, respectively. For the groundwaters, the points which are on or under the regression curve (or evaporation line) suggest that evaporation has lowered δD in the surface water prior to infiltration into groundwater.[40] Except for the samples along the H1 profile, most points fall under the LMWL, suggesting that evaporation was strong before rainfall recharged the groundwater.

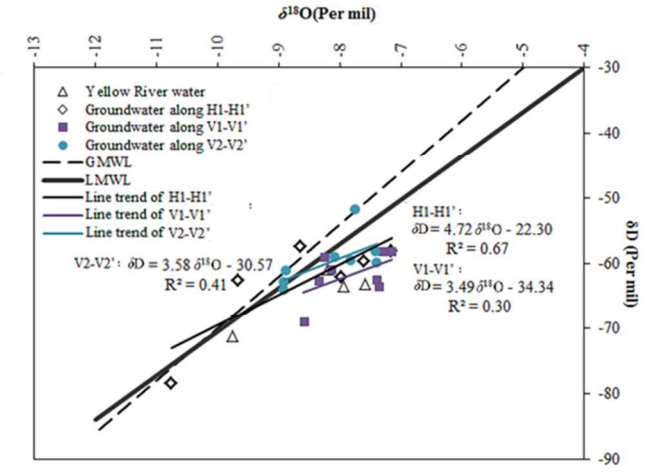

Fig.10 Stable isotope characteristics along the hydrogeological profiles

Other anthropogenic activities

The observed maximums in groundwater NO_3^- may be caused by local anthropogenic activities.[16] Wastewater irrigation is common in many counties with arid or semi-arid regions. Wastewater irrigation usually occurs in suburban areas, which play an important role in groundwater storage and exploitation. The average wastewater load of irrigated croplands in the NCP was 3276 m^3/ha/year.[14] With increased urbanization, the amount of wastewater increased sharply in cities, and groundwater was threatened by huge volumes of non-treated wastewater. When wastewater is applied to land, some of these constituents are removed as the wastewater

moves through the soil, and organic nitrogen is converted to NO_3^-.[14, 33]

4. Conclusions

This study quantified the NO_3^- content, analyzed the factors that influence the spatial distribution of NO_3^-, and concluded the effects of long-term Yellow River irrigation practices on NO_3^- pollution in the surface water and groundwater of the Piedmont of South Taihang Mountains. The main conclusions of this study are:

(1) Resulting from alkaline conditions and lixiviation, groundwater in the study region exhibited higher EC and more complex saline conditions than that in surface water.

(2) Pollution of NO_3^- in groundwater was slightly higher than in surface water. It is worth noting that the magnitude of NO_3^- in groundwater was more serious than that in NCP.

(3) The spatial distribution of NO_3^- in groundwater was closely related to the groundwater flow system, whilst the groundwater sites with higher NO_3^- concentrations did not overlap with the spatial distribution of fertilizer consumption.

(4) Groundwater sources have been affected by the seepage along Yellow River, and the apparent surface water - groundwater interactions which have been influencing the spatial distribution of NO_3^- in the Piedmont of South Taihang Mountains.

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Notes

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