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Water quality assessment in the rivers along the water conveyance system of the Middle Route of the South to North Water Transfer Project (China) using multivariate statistical techniques and receptor modeling

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ABSTRACT

A total of 190 grab water samples were collected from 19 rivers along the water conveyance system of the Middle Route of China's interbasin South to North Water Transfer Project (MRSNWTP). Multivariate statistics including principal component/factor analysis (PCA/FA), analysis of variance (ANOVA), and cluster analysis (CA) were employed to assess water quality, and the receptor model of factor analysis-multiple linear regression (FA-MLR) was used for source identification/apportionment of pollutants from natural processes and anthropogenic activities to river waters. Our results revealed that river waters were primarily polluted by COD_{Mn}, BOD, NH_4^+-N, TN, TP, and Cd with remarkably spatio-temporal variability, and there were increasing industrial effluents in rivers northward. FA/PCA identified four classes of water quality parameters, i.e., mineral composition, toxic metals, nutrients, and organic pollutants. CA classified the selective 19 rivers into three groups reflecting their varying water pollution levels of moderated pollution, high pollution, and very high pollution. The FA-MLR receptor modeling revealed predominantly anthropogenic inputs to river solutes in Beijing and Tianjin, i.e., 77% of nitrogen and 90% of phosphorus from industry, and 80% of COD_{Mn} from domestics. This study is critical for water allocation and division in the water-receiving areas using the existing rivers for MRSNWTP.

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1. Introduction

The impressive growths of human populations and economic development have resulted in the current worldwide deterioration in water quality, particularly the elevation of certain nutrients leading to eutrophication and heavy metals in the aquatic environment [1–8]. Natural processes and anthropogenic activities such as precipitation and soil erosion, and domestic consumptions, industrial and agricultural activities largely contribute to chemical pollutants in the fluvial systems [2,9,10], and diffuse sources by agricultural runoff have been increasingly of great concern for nutrients due to widely fertilizer overuse. Meanwhile, industrial developments, particularly electroplating, metallurgy, mining and mineral processing, have been changing the biogeochemical cycles of heavy metals [1,4]. Recent studies have also revealed that urban development and hydrological impacts by climate change greatly degraded water quality [11,12].

Water pollution by nutrients and heavy metals contributes to biodiversity loss, environmental degradation, and human health hazard [13,14]. Intake of considerable amounts of metals could result in varying life threatening cancers and mental disease, e.g., Cd could cause kidney damage and cardiovascular disease [14]. Meanwhile, excessive nutrients can lead to water eutrophication, causing a hypoxia environment, the reductions of species diversity and microbial growth, mortality of benthic communities, and stress in fishery resources [14]. Studies have indicated that many rivers/streams particularly in developing countries are heavily polluted due to industrial and municipal wastewater, as well as agricultural runoff [3,4,6,15], for example, tributaries in the Changjiang system [5–8], Gomti River in India [4], the Han River in South Korea [16,17], Dil Deresi stream in Turkey [15], Pisuerga River in Centre-North Spain [3], and a few rivers in Chile [18].

Despite that there are numerous studies on spatial and temporal variability in water quality in river systems [i.e., [3,6,7,17]], many studies investigated either spatial variations of water quality or temporal trends for a few selected sites [i.e., [3,7]], while others tended to be simply exercises in statistics [i.e., [19,20]]. Chang et al. [17] and Pizarro et al. [18] provided good cases on spatial and

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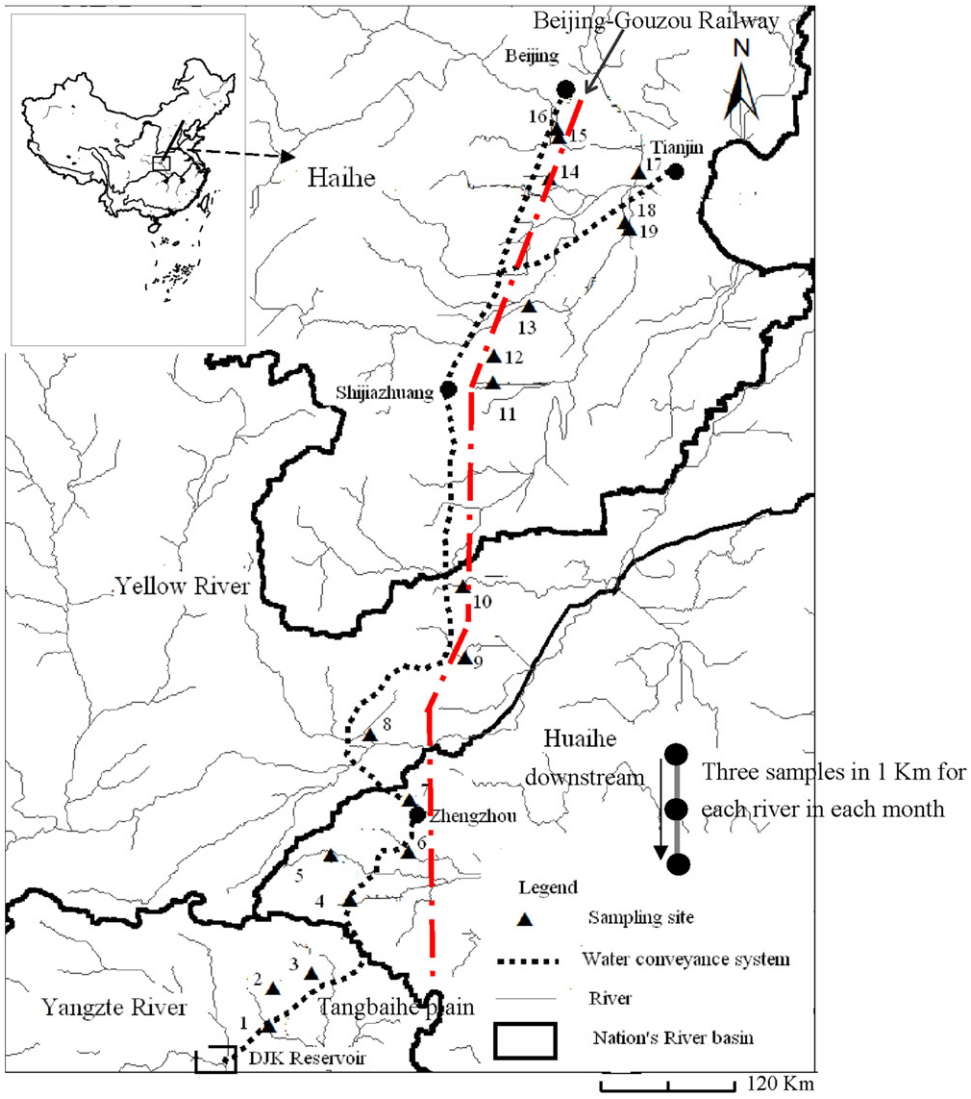

Fig. 1. Locations of sampling sites along the water conveyance system of the Middle Route of the South to North Water Transfer Project, China (these selective rivers are within the four large basins of Changjiang, Huaihe, Yellow and Haihe Rivers).

temporal patterns of water quality; however, they did not quantify source profiles of pollutants. In fact, source contribution could help to verify the relations between landscape and water quality, as well as implement pollution management policies.

A number of receptor-oriented source apportionment models have been developed to quantify the contributions of various sources to measured pollutants. The most widely used models included multiple linear regression with factor analysis (FA-MLR) [21], positive matrix factorization (PMF) [22], U.S. Environment Protection Agency UNMIX [23], and chemical mass balance (CMB) [24]. The CMB model requires detailed knowledge of source types. Three multivariate receptor models (FA-MLR, PMF and UNMIX) can simultaneously analyse a series of observations and quantitatively assess the contributions of various sources to each observation without prior knowledge about number and nature of sources [25]. These models have been well-documented on assessment of air pollutants [21,24–27]; however, studies on river quality concentrated on qualitatively potential pollutant sources [i.e., [3,7,19,28,29]]. Recently, FA-MLR has been successively applied in source apportionment of heavy metals in surface waters [4,15,30]. In our study, the eigenvector model, FA-MLR, relatively simple and easily performed using common software package, was therefore used for large variety of water variables.

China possesses the total water resources of 2800 billion m^3, ranking the sixth in the world, but only 2300 m^3 of water occupation per capita, amounting to only 1/4 of the world's average. The uneven spatial distribution of water resources and water pollution further complicate the water shortage particularly in the Northwest and Northern China. The Changjiang River (Yangtze) basin and southern China, with a cultivated land of less than 40%, yields a runoff accounting for more than 80% of the national total. Conversely, the Yellow River, Huaihe River, Haihe River basins and northwest inland have half of national total area and 45% of total cultivated land and 36% of the total population, but only possess less than 12% of the total water resources [31–33].

Since 2002, China has been implementing the three-route South–North Water Transfer Project (i.e., East, Middle and West) (SNWTP), transferring water from the water-rich Yangtze River to Northwest and North China. The Middle Route, with a total length of 1230 km, will divert 13 billion m^3 per year of water from the upper Han River to the North China Plain including the municipalities of Beijing and Tianjin. The water conveyance system, crossing Henan, Hebei, Beijing and Tianjin, intersects four large rivers of

China including the Yangtze, Huaihe, Yellow and Haihe Rivers (Fig. 1). Research studies in relation to the interbasin water transfer project have been focused on water quality [5–9,34,35] and the relations between land use/land cover and water chemistry [10,36] in the water source area (the upper Han river), and demonstrated chemical pollutants including nitrogen, chemical oxygen demand (COD_{Mn}) and several heavy metals in the Han river. However, water quality and associated source identification and apportionment in the rivers along the water conveyance system is unavailable. This information is critical for water allocation and division in the water-receiving areas using the existing rivers.

The present study was carried out to firstly investigate water quality in the rivers along the water conveyance canal of the Middle Route of SNWTP (MR-SNWTP). The objectivities of the study were to (1) assess the spatial and temporal patterns of water quality in the rivers using multivariate statistical analyses, and (2) quantify natural and anthropogenic sources to water pollution in the rivers using the receptor model of FA-MLR. The results were expected to fill the knowledge gap of water contamination status, distribution and source apportionment of chemical pollutants in rivers along the canal system and ultimately help develop water management and conservation strategies in the water-receiving areas of the interbasin water transfer project.

2. Materials and methods

2.1. Study area

The water conveyance system of MR-SNWTP (canal system), ca. 1230 km long, starting at the Danjiangkou Reservoir, goes across the Tangbaihe plain, and passes through the pediment plain and the south foot of the Funiu Mountain (Fig. 1). It then crosses the Yellow River in the west of Zhengzhou city, goes further northward along the pediment plain at the east foot of the Taihang Mountain and the west side of the Beijing–Guangzhou Railway and finally reaches its destiny of Beijing and Tianjin [31].

The water-receiving region of the MR-SNWTP is affected by the continent monsoon climate with subtropic and warm temperate zones, the annual rainfall decreases from south to north (800–400 mm). There is large inter- and intra-annual variability in precipitation, and the flood season occurs in July, August and September (80% of the annual total in south). Meanwhile, evaporation capacity increases from 1073 mm (Tanbaihe Plain) to 1190 mm (Haihe basin) northward due to transformation of humid-subtropic to semi-arid warm temperate climate. The annual mean temperature is 11.5–14.9 °C with an increase of 0.02–0.04 °C/yr, and the highest and lowest daily values of 40 °C and −27.4 °C in a period of 1951–2000, respectively.

Water-receiving region of the water transfer project covers a total area of approximately 150,000 km^2 and includes four metropolises such as Zhengzhou, Shijiazhuang, Beijing and Tianjin, and other 19 medium-sized cities. Thus, the region is highly urbanized with rapid economic development in the past decade, resulting in large amount of waste water discharges and chemical oxygen demand (COD) (Fig. 2). Waste water (together industrial and domestic) and COD_{Mn} discharges in the region account for about 12% and 11% of the nation's total, respectively [37]. There is intensive land utilization along the canal system, indicated by 78.7% of agriculture and 2.2% of urban, respectively in an area of 6110 km^2 along the water conveyance system of the MR-SNWTP. Vegetated land including forest and shrub covers about 7.1% and others including grass lands and waters together account for about 12% of the total land area (Fig. 3) [38]. Agriculture is more intense in the Henan and Hebei provinces while industry is much more developed in Beijing and Tianjin.

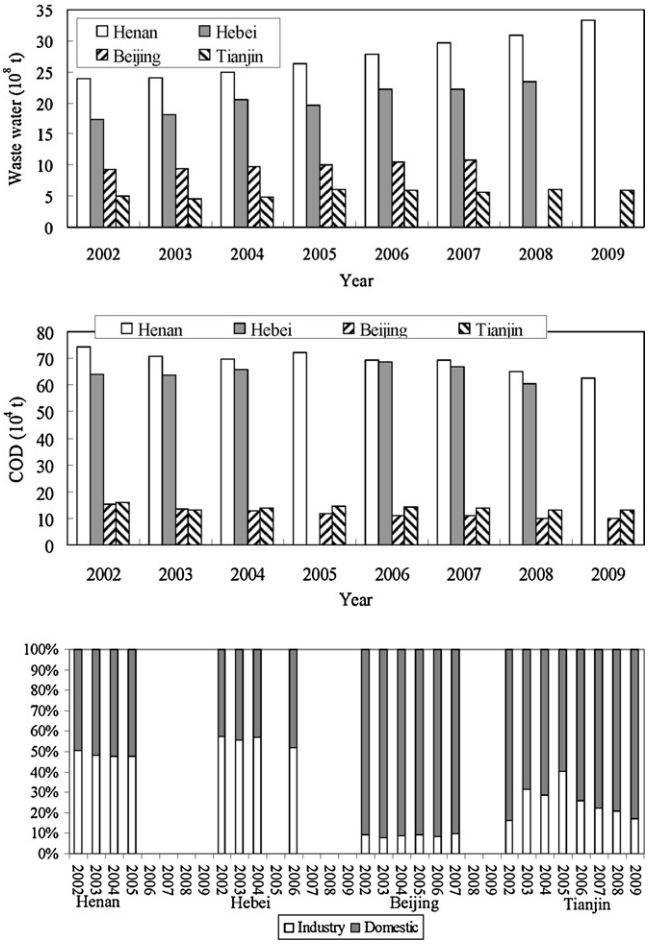

Fig. 2. Waste water, COD discharges and relative importance of industrial and domestic contributions to COD from 2002 to 2009 in Henan, Hebei, Beijing and Tianjin, respectively.
Source: [37].

2.2. Sampling and analysis

Four sampling campaigns were conducted in 19 rivers along the canal system of the MR-SNWTP during 2006–2007 (September and December 2006, and April and June 2007), and there were 10 rivers in Hennan, four rivers in Hebei, two rivers in Beijing and three rivers in Tianjin, respectively (Table 1; Fig. 1). Three water samples in a distance of 1 km from upper to downstream in each river were

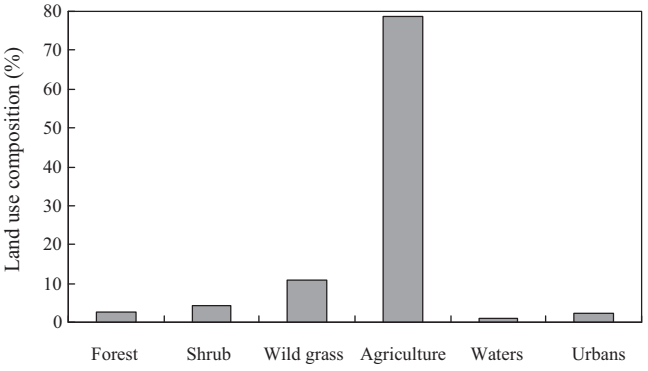

Fig. 3. Land use/land cover composition in an area of 6110 km^2 along the water conveyance system of the MR-SNWTP.
Source: [38].

Table 1
Rivers and geo-locations of sampling site along the water conveyance canal.

No.	River	Province	a.s.l (m)	Longitude	Latitude
Yangtze					
1	Tuanhe	Henan	123	112°07.469′	32°42.078′
2	Zhaohe	Henan	173	112°10.631′	33°00.049′
3	Yahe	Henan	153	112°37.973′	33°17.059′
Huaihe					
4	Shahe	Henan	126	112°55.978′	33°42.785′
5	Beiruhe	Henan	99	112°13.523′	33°55.299′
6	Yinhe	Henan	116	112°32.591′	33°07.007′
7	Jialuhe	Henan	106	113°46.643′	34°50.553′
Yellow					
8	Qinhe	Henan	99	113°23.998′	35°03.317′
9	Qihe	Henan	75	114°16.899′	35°36.239′
10	Weihe	Henan	65	114°21.706′	35°31.195′
Haihe					
11	Zhihe	Hebei	51	114°33.746′	37°22.521′
12	Jiaohe	Hebei	65	114°30.234′	37°55.222′
13	Taipinghe	Hebei	67	114°31.188′	38°06.518′
14	Menglianghe	Hebei	61	114°54.635′	38°29.887′
15	Liulihe	Beijing	21	116°01.378′	39°36.208′
16	Yongdinghe	Beijing	88	116°16.147′	39°52.879′
17	Beiyunhe	Tianjin	10	117°03.596′	39°22.257′
18	Duliujian	Tianjin	18	117°00.959′	39°01.358′
19	Ziyahe	Tianjin	28	117°00.951′	39°01.359′

collected. Ultimately, a total of 190 grab water samples, taken at a depth of approximate 10 cm using previously acid-washed 5 l high density polyethylene (HDPE) containers, were pretreated for laboratory measurements. A 1000 ml sub-sample was filtered through pre-washed 0.45 μm Millipore nitrocellulose filters. The initial portion of the filtrate was discarded to clean the membrane and the following ones were stored using previously acid-washed HDPE bottles. The two aliquots, one acidified to pH 2 using ultra-pure concentrated nitric acid for metal determination and another non-acidified for the anions measurements were prepared. The rest samples were acidified by concentrated sulfuric acid for the determination of biochemical oxygen demand (BOD), chemical oxygen demand (COD_{Mn}), total nitrogen (TN), and total phosphorus (TP). All samples were stored in a fridge at 4 °C before analysis, and the analytes were finished in the two weeks after the 10-day field work.

Water temperature (T), dissolved oxygen (DO), pH, oxidation-reduction potential (ORP), electrical conductivity (EC), total dissolved solid (TDS), turbidity, and ammonium-nitrogen (NH_4^+-N) of water samples were detected *in situ* using multiparameter water quality monitoring instrument (YSI Incorporated, Yellow Springs, Ohio, USA). Calibration of sensors was performed before every survey. The membranes used for filtration were dried at 63 °C to constant mass, and total suspended solid (TSS) was calculated from the difference in the filter paper weights before and after filtering. Bicarbonate (HCO_3^-) was titrated using hydrochloric acid on the sampling day, while chloride (Cl^-), sulfate (SO_4^{2-}) and hardness (Hard) were determined in laboratory by titration using silver nitrate, barium chromate and EDTA, respectively. BOD was the differences of dissolved oxygen of the samples before and after the 5-day incubation at 20 °C in a biochemistry incubator, and COD_{Mn} was analysedanalysed by potassium permanganate method. TP was analysedanalysed by digestion and a colorimetric method (ammonium molybdenum blue method/ascorbic acid method) after the samples were digested with concentrated nitric and sulfuric acids. The concentration of the TN was determined by alkaline potassium persulfate oxidation-UV spectrophotometric method. Heavy metals including Cu, Zn, Cd, Mn, and Fe were determined using flame atomic absorption spectrometry (FASS; WYX-9004). All the procedures were strictly following Chinese State Environment Protection Bureau (CSEPB) [39]. Quality control procedures, including internal quality control using reference materials, were employed to prove the validity of the measured results.

2.3. Statistical analyses

Multivariable statistic approach, including factor and principal component analyses (FA/PCA) has been widely used to characterize spatial and temporal variations [4,7,8], and they are capable of exploring the hidden complex and relations between features in a data set through reducing the dimensionality of the data set. This reduction generates new orthogonal (non- correlated) variables, and the principal components (PCs) are arranged in a descending order of importance for explaining variance of all original property. FA further reduces the contribution of variables with minor significance obtained by PCA and the new group of variables called varifactors (VFs) are extracted through varimax rotated PCA. These reduced PCs/VFs can describe a large set of original variables without losing much information [3,4,28,29] and the PCs/VFs can be interpreted as origins or common sources of environmental pollutants. Cluster analysis (CA) is an unsupervised pattern recognition approach and classifies objects into categories or clusters on the basis of similarities and dissimilarities of samples. In the present study, Q-model hierarchical agglomerative CA without any prior knowledge of number of clusters was performed on the normalized data set by means of the Ward's method using squared Euclidean distance as a measure of similarity [3,4]. One way analysis of variance (ANOVA) was employed to compare the seasonal and spatial differences of water quality variables ($p < 0.05$; least-significance difference, LSD). All the statistical procedures were conducted using statistical product and service solution (SPSS) 15.0 for Windows.

2.4. Receptor modeling (FA-MLR)

After determination of possible sources influencing the river water quality using PCA/FA, a receptor modeling based on multiple linear regression of factor score (FA-MLR) was used to quantify the contribution of each pollutant. Detailed description including operating principle and procedures about the FA-MLR model could be found in Thurston and Spengler [21] and Guo et al. [26]. This

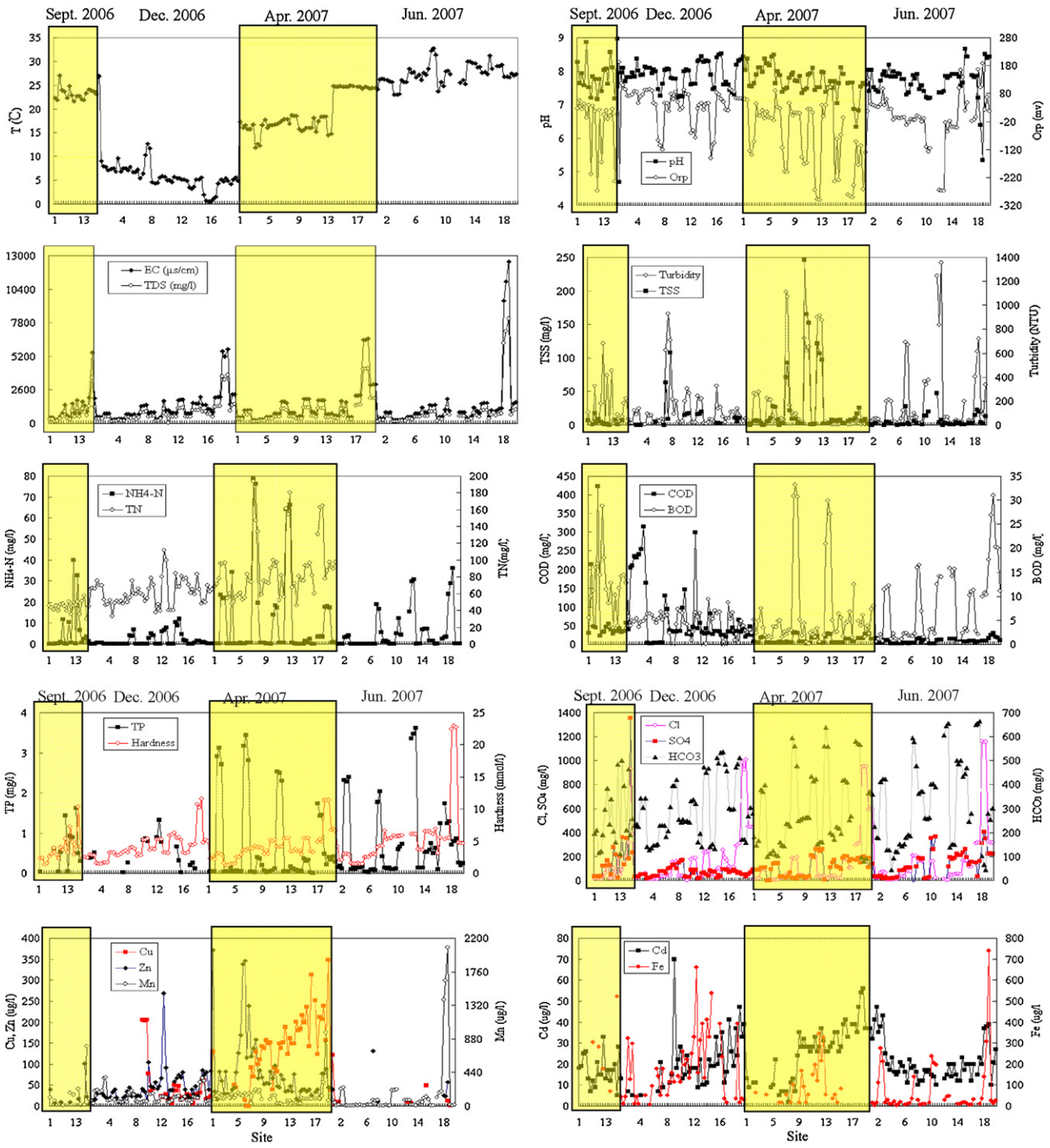

Fig. 4. Spatial and temporal variability of water quality in the selective 19 rivers along the water conveyance system of the MR-SNWTP.

multivariate receptor model, conducted in SPSS software, used the absolute factor scores as independent variables, while the chemical concentrations as the dependent variables.

3. Results and discussion

3.1. Seasonal and spatial variations of water quality

Water quality variables including physico-chemicals, nutrients, major inorganic matters, and heavy metals were illustrated in Fig. 4 and Table 2. pH varied between 4.7 and 9 with water acidification in sites 1 and 18. Orp varied from −301 to 191 mV and the 95% confidence interval for the average was −27 to 4 mV. EC and TDS showed the similar trends and their maximum concentrations occurred in site 18. TSS and turbidity seemed to have higher concentrations in the intermediate sites, averaging 85.3 mg/l and 28.7 NTU, respectively. NH_4^+-N and TN displayed highest concentrations in site 7. COD_{Mn} had its highest concentration (424 mg/l, site 5) in September, and BOD exhibited the highest concentration (33 mg/l, site 7) in April, while TP and hardness in summer. Heavy metals tended to increase northward. Furthermore, variables such as pH, EC, TDS, nitrogen, turbidity, COD_{Mn}, BOD, Cd and Fe of three transverse sections in a distance of 1000 m of the same river exhibited

Table 2
Seasonal concentrations (mean values with standard errors (S.E.)) for water quality of rivers along the canal system, as well as comparison with environmental quality standards for surface water (GB3838-2002) in China.

	September 2006			December 2006			April 2007			June 2007			Total[a]			Grade				
	n	Mean	S.E	*n*	Mean	S.E	*n*	Mean	S.E	*n*	Mean	S.E	Mean ±S.E	Min	Max	I	I	III	IV	V
T (°C)	19	23.41	0.35	57	5.64	0.32	56	19.08	0.54	53	27.34	0.29	17.8 ± 0.7	0.5	32.8					
EC (μs/cm)	19	1249.05	269.96	57	1282.26	153.09	56	1380.68	191.28	53	1425.06	333.54	1349.6 ± 123.6	244	12527	750[b]				
TDS (mg/l)	19	811.11	174.85	57	822.58	100.57	56	902.05	124.42	53	927.77	216.72	875.6 ± 80.4	66	8141					
pH	19	7.87	0.12	57	7.84	0.07	56	7.73	0.05	53	7.69	0.07	7.8 ± 0.04	4.7	8.97	6–9				
Orp (mV)	19	−30.74	23.59	57	41.31	8.93	56	−68.46	16.45	53	0.02	12.71	−11.1 ± 7.8	−300.9	191.3					
Turb (NTU)	19	27.62	7.74	57	21.68	4.09	56	30.39	7.15	53	34.71	7.47	28.7 ± 3.4	0	242					
TSS (mg/l)	13	27.86	7.73	20	90.17	32.22	56	136.73	36.53	44	34.45	7.75	85.3 ± 16.8	0	1380					
COD_{Mn} (mg/l)	19	68.09	21.91	57	69.03	10.74	56	11.8	1.17	53	8.5	0.83	34.3 ± 4.5	1.7	424	15	15	20	30	40
BOD (mg/l)	19	12.07	1.33	57	4	0.39	56	6.21	1.11	53	7.53	1.03	6.5 ± 0.5	0	33	3	3	4	6	10
NH_4^+-N (mg/l)	19	5.9	2.59	57	1.7	0.39	56	10.76	2.74	53	5.29	1.26	5.9 ± 1	0.01	78.7	0.15	0.5	1	1.5	2
TN (mg/l)	19	44.48	1.52	57	61.45	2	56	88.36	4.71				70.4 ± 2.6	29.72	193.68	0.2	0.5	1	1.5	2
TP (mg/l)	11	0.63	0.17	17	0.51	0.09	56	0.64	0.14	53	0.73	0.13	0.66 ± 0.08	0	3.62	0.02	0.1	0.2	0.3	0.4
Hard (mmol/l)	19	3.79	0.49	57	4.04	0.27	56	4.17	0.29	53	5.32	0.63	4.4 ± 0.2	1.25	22.9	4.5[b]				
Cl^- (mg/l)	19	145.85	50.21	57	157.96	29.89	56	152.61	31.86	53	162.41	36.34	156.4 ± 17.5	2.6	1159.4	250[b]				
SO_4^{2-} (mg/l)	19	213.25	67.79	57	65.54	4.78	53	117.04	10.4	49	141.76	15.36	117.6 ± 9.5	1.49	1353.5	250[b]				
HCO_3^- (mg/l)	19	266.81	28.82	57	292.42	16.64	56	289.38	21.3	53	319.7	25.41	296.7 ± 11.4	43.9	665.1	300[b]				
Cu (mg/l)				30	0.05	0.01	46	0.14	0.01	11	0.01	0	0.09 ± 0.01	ND	0.35	0.01	1	1	1	1
Zn (mg/l)	9	0.02	0.01	57	0.04	0.01	56	0.08	0.01	5	0.05	0.02	0.06 ± 0.006	ND	0.37	0.05	1	1	2	2
Cd (mg/l)	19	0.02	0	42	0.02	0	56	0.02	0	53	0.02	0	0.02 ± 0.001	ND	0.07	0.001	0.005	0.005	0.005	0.01
Mn (mg/l)	9	0.17	0.08	57	0.12	0.01	53	0.13	0.02	53	0.15	0.05	0.13 ± 0.02	0.01	2.08	0.1[b]				
Fe (mg/l)	5	0.27	0.07	45	0.17	0.02	23	0.1	0.02	50	0.06	0.02	0.12 ± 0.01	ND	0.74	0.3[b]				

Grade I: clean water from headwater and national conservation area that can be used for domestic purposes after simple disinfection, for recreational purposes and irrigation. Grade II: fairly clean water that can be used as domestic water after treatment, for recreational purposes, for fish farming etc., and the area is strictly protected. Grade III: water also can be used for domestic, recreational purposes after suitable treatment. Grade IV: polluted water which can only be used as industrial water after treatment. Grade V: heavily polluted water that should not be used at all.

[a] Total average; ND, lower than detection limit.

[b] Maximum desirable concentration.

Table 3
Comparison of water quality in the present study with other rivers.

	China				India[d]		Han River, South Korea[e]		Turkey[f]	Spain[g]	Chile[h]
	Our study	Han River[a]	Jinshui River[b]	Yangtze[c]	Gomti River	Patancheru industrial town	Gurogongdan	Yangjae	Dil Deresi	Pisuerga River	Elqui
T (°C)	17.8	21.3			26.7		17.3	14.6		14.3	
EC (μs/cm)	1349.6	285.6			421.71		727	462		629	
TDS (mg/l)	875.6	185.3	137.3		264.22	2608.5				427	
pH	7.8	8.2	7.8		8.35	7.8	7.3	7.6		7.6	
Orp (mV)	-11.1	60.3									
Turb (NTU)	28.7	31.1	3.2								
TSS (mg/l)	85.3	26.8			42.7		70.3	10.3			
COD_{Mn} (mg/l)	34.3	2.5	1.7		16.09		51	8.6		5	
BOD (mg/l)	6.5	1.1			5.16		95.8	9.7		3.7	
NH_4^+-N (mg/l)	5.9	0.3	0.17		0.17					1.3	
TN (mg/l)	70.4			1.95	2.82		27.2	11.4			
TP (mg/l)	0.66		0.12	0.07	0.22		3.9	0.5			
Hard (mmol/l)	4.4	1.3	1		1.8					2.6	
Cl^- (mg/l)	156.4	6.3	5.68		12.34					28.3	
SO_4^{2-} (mg/l)	117.6	32.1	19.72		18.41					112.7	445.7
HCO_3^- (mg/l)	296.7	148	109.8							156.1	
Cu (mg/l)	0.09	0.013	0.01	0.0084	0.042				0.037		6.1
Zn (mg/l)	0.06			0.019	0.121	0.099			0.7		
Cd (mg/l)	0.02	0.002		0.0003	0.001				0.008		0.028
Mn (mg/l)	0.13	0.031			0.161	0.073				0.04	
Fe (mg/l)	0.12	0.031	0.17	1.66	4.98	0.16			4.03	0.11	
Reference		[5,7]	[41]	[42,43]	[4]	[20]	[16]	[16]	[15]	[3]	[18]

[a] Han River is the water source area of the MR-SNWTP.
[b] The Jinshui River is located in the headwater of the Han River, China.
[c] Yangzte: N and P in Nanjing section from Muller et al. [42]; while metals from Wang et al. [43].
[d] Polluted rivers in industrial areas.
[e] Sampling sites locating in Seoul, South Korea.
[f] Polluted rivers in industrial areas.
[g] Polluted rivers in industrial areas.
[h] Very high-polluted.

large differences, and these sampling sites (i.e., sites 18 and 19) were primarily distributed in the Haihe River near Beijing and Tianjin city. Compared to China's environmental quality standards for surface water (GB3838-2002) [[40]; Table 2], rivers were heavily polluted by COD_{Mn}, BOD, NH_4^+-N, TN, TP, and Cd.

By comparing with results in the water source area of the MRSNWTP, abroad rivers (Table 3), and world averages (i.e., 1 μg/l for Cu, 10 μg/l for Zn, 0.02 μg/l for Cd and 6 μg/l for Mn) [44], chemical species along the canal system had considerably higher mean concentrations. The concentration of COD_{Mn} in our study was ca. 14 times higher than in the upper Han River (China), 20 times higher than in an unpolluted river (the Jinshui River in China). This could be explained by high vegetated coverage of 77% in the upper Han river, 96% for the Jinshui River [5]. COD_{Mn} was even two times higher than in the Gomti River in India, four times higher than in the Han River (Seoul, Korea), and seven times higher than the polluted river in Spain. TN concentration in the considered region was 35 times higher than in the Yangtze, 25 times higher than in the Gomti River in India, 2.6 times higher than in the high polluted section in the Han River in South Korea. Considering the priority toxic pollutants, i.e,

Table 4
ANOVA for water quality in each sampling time along the canal system, China.

	Sum of squares	df	Mean square	F	p-value
T	13945.49	3	4648.50	551.03	0.000
EC	806392.72	3	268797.57	0.09	0.963
TDS	422730.79	3	140910.26	0.12	0.951
pH	0.84	3	0.28	1.14	0.334
Orp	354647.83	3	118215.94	12.42	0.000
Turbidity	4910.69	3	1636.90	0.77	0.513
TSS	305207.65	3	101735.88	2.84	0.041
COD_{Mn}	154064.25	3	51354.75	17.27	0.000
BOD	1006.40	3	335.47	7.77	0.000
NH_4^+-N	2346.44	3	782.15	4.68	0.004
TN	35397.21	2	17698.61	27.84	0.000
TP	0.65	3	0.22	0.26	0.852
Hard	62.23	3	20.74	2.22	0.087
Cl^-	4965.38	3	1655.13	0.03	0.993
SO_4^{2-}	356919.84	3	118973.28	8.29	0.000
HCO_3^-	49064.68	3	16354.89	0.68	0.565
Cu	0.22	2	0.11	25.42	0.000
Zn	0.05	3	0.02	4.72	0.004
Cd	0.00	3	0.00	0.82	0.485
Mn	0.05	3	0.02	0.27	0.845
Fe	0.40	3	0.13	7.56	0.000

df: degrees of freedom. Significance at $p < 0.05$.

Table 5
Varimax rotated factor loadings for water quality parameters in the four sampling seasons (the significance of Kaiser–Meyer–Olkin (KMO) and Bartlett's sphericity test is <0.001).

September 2006	Component				Communality	December 2006	Component					Communality
	1	2	3	4			1	2	3	4	5	
Orp	−**0.59**	−0.18	0.19	−0.48	0.65	Orp	0.03	−0.45	−**0.62**	**0.45**	−0.18	0.84
EC	**0.98**	0.09	−0.02	0.11	0.98	EC	**0.98**	0.04	0.02	−0.07	−0.09	0.98
TDS	**0.98**	0.09	−0.02	0.11	0.98	TDS	**0.97**	0.04	0	−0.07	−0.09	0.95
Turbidity	0.03	0.01	−0.04	**0.89**	0.79	Turbidity	0.06	0.11	**0.87**	−0.14	0.24	0.84
COD_{Mn}	−0.1	−0.16	−0.17	−**0.53**	0.34	COD_{Mn}	−0.22	−0.19	−0.03	**0.87**	0.19	0.88
BOD	−0.11	−0.08	−**0.91**	0.06	0.84	BOD	−0.26	−0.37	−**0.72**	−0.08	0.22	0.78
NH_4^+-N	0.21	**0.77**	0.35	0.24	0.81	NH_4^+-N	0.1	**0.86**	0.06	−0.13	0.24	0.82
TN	−0.42	**0.54**	−0.07	0.25	0.54	TN	−0.02	**0.8**	0.35	0.06	−0.08	0.78
Hard	**0.93**	0.29	0.05	0.02	0.95	Hard	**0.93**	0.21	−0.1	−0.12	−0.01	0.94
Cl^-	**0.93**	−0.05	0.01	0.09	0.88	Cl^-	**0.94**	−0.04	0.08	−0.05	−0.27	0.96
SO_4^{2-}	**0.94**	−0.17	−0.13	−0.01	0.93	SO_4^{2-}	−0.19	−0.34	0.48	−0.61	0.21	0.79
HCO_3^-	0.14	**0.93**	0.06	−0.02	0.88	HCO_3^-	−0.07	**0.78**	0.32	−0.05	0.1	0.74
Cd	−0.34	0.15	**0.74**	0.21	0.73	Zn	0.31	**0.68**	0	−0.04	−0.24	0.62
						Mn	**0.83**	0.07	0.29	0.22	0.24	0.88
						Cd	0.15	−0.08	−0.18	−0.07	−**0.83**	0.76
						Fe	0.07	**0.64**	−0.36	0.03	0.46	0.76
Eigenvalue	5.41	2.51	1.34	1.06		Eigenvalue	5.24	3.66	2.1	1.29	1.06	
Cumulative %	40.54	55.66	67.9	79.37		Cumulative %	28.98	50.56	65.44	74.56	83.35	

April 2007	Component					Communality	June 2007	Component			Communality
	1	2	3	4	5			1	2	3	
Orp	−0.41	−**0.73**	−0.33	−0.18	0.18	0.87	Orp	0.33	−**0.77**	0.33	0.81
EC	**0.97**	0.12	0.14	0.03	0.01	0.98	EC	**0.96**	−0.05	0.21	0.97
TDS	**0.97**	0.12	0.14	0.03	0.01	0.98	TDS	**0.96**	−0.05	0.21	0.97
Turbidity	−0.08	**0.69**	−0.21	**0.60**	0.27	0.96	Turbidity	0.33	**0.86**	0.05	0.84
TSS	0.02	0.38	−0.01	**0.87**	0.12	0.91	TSS	0.47	**0.55**	−0.12	0.54
COD_{Mn}	0.59	**0.72**	−0.01	0.22	0.19	0.95	COD_{Mn}	**0.83**	0.40	−0.08	0.86
BOD	−0.09	**0.84**	−0.19	0.00	0.39	0.90	BOD	**0.77**	0.44	−0.02	0.79
NH_4^+-N	0.11	**0.80**	−0.20	0.31	0.30	0.88	NH_4^+-N	**0.66**	**0.64**	0.18	0.87
TN	0.10	**0.94**	0.06	0.07	−0.06	0.91	TP	0.01	**0.93**	0.18	0.89
TP	−0.08	−0.14	−0.32	−0.21	−**0.83**	0.86	Hard	**0.95**	0.03	0.08	0.91
Hard	**0.94**	0.07	0.22	0.03	−0.02	0.94	Cl^-	**0.94**	−0.11	0.16	0.92
Cl^-	**0.94**	0.00	0.19	−0.07	−0.03	0.92	SO_4^{2-}	**0.73**	−0.27	−0.50	0.85
SO_4^{2-}	0.24	−0.49	**0.55**	0.28	−0.38	0.82	HCO_3^-	−0.26	**0.67**	−0.33	0.62
HCO_3^-	−0.17	**0.90**	0.18	0.15	−0.11	0.90	Mn	**0.94**	−0.01	0.28	0.97
Cu	0.16	0.04	**0.73**	−0.34	0.32	0.78	Cd	0.32	−0.15	**0.84**	0.83
Zn	0.03	−0.06	−**0.84**	−0.05	−0.09	0.71	Fe	**0.78**	0.12	0.20	0.67
Mn	**0.74**	−0.16	−0.30	−0.03	0.10	0.67	Eigenvalue	8.34	3.73	1.23	
Cd	0.55	−0.09	**0.73**	−0.03	−0.01	0.85	Cumulative %	49.97	73.86	83.16	
Eigenvalue	6.32	5.13	2.14	1.14	1.09						
Cumulative %	28.74	56.72	71.43	80.19	87.80						

Extraction method: Principal component analysis. Rotation method: Varimax with Kaiser normalization.

Cd, Cu, and Zn presented in US EPA, 2006 for aquatic life protection [45], their mean values showed that Cu concentration was about 90 times as high as world average, Zn was six times, and Cd was 100 times. Further, Cd concentration was evidently higher (3–67 times) than both home and abroad rivers, and comparable to a very high-polluted river by industrial effluents in Chile. Thus, surface water in the water-receiving region (North China) was highly polluted and therefore lost their natural ecosystem service function.

Analysis of variance indicated remarkable seasonal differences for water temperature, Orp, TSS, COD_{Mn}, BOD, NH_4^+-N, TN, SO_4^{2-}, Cu, Zn, and Fe, and the maximum concentrations of COD_{Mn}, BOD, SO_4^{2-} and Fe occurred in autumn (Sept. 2006), while other variables showed their maximum concentrations in spring (Apr. 2007) (Tables 2 and 4). Due to highly urbanization along the canal, municipal and industrial wastes are primarily responsible for water pollution. In September and June (wet season), large amounts of rain runoff showed diluted effects though agricultural activities, partly contributed to riverine nutrients in Henan and Hebei. However, drought in the period from October to May together with large amounts of industrial and domestic waste water resulted in highest monthly nitrogen concentration in spring. This was confirmed by industrial markers of metals, i.e., highest concentrations of Cu and Zn (Table 2). Result indicated that waters in varying sampling time were always polluted by COD_{Mn}, BOD, NH_4^+-N, TN, TP and Cd (Table 2), reflecting intense anthropogenic activities particularly industrial effluents, e.g., waste water in Henan was 33×10^8 t/yr, 23×10^8 t/yr for Hebei, 11×10^8 t/yr for Beijing and 6×10^8 t/yr for Tianjin, respectively (Fig. 2). This was understandable considering more than 20 cities are located along the water conveyance system.

FA/PCA extracted four, five, five and three principal components (PCs) for the measurement data in September and December 2006, and April and June 2007, respectively, and these PCs with eigenvalue >1 explained 79%, 83%, 88% and 83% of the total variance in the respective data sets (Table 5). For the data set pertaining to September 2006, the first principal component (PC1) explained 40.5% of the total variance and had strong positive loadings on EC, TDS, Hard, Cl^- and SO_4^{2-} and moderate negative loadings on Orp, which could be interpreted as a mineral component of the river water [3,4]. These variables had a common origin in rock dissolution (limestone) and soils, and high Cl^- and SO_4^{2-} also indicated anthropogenic inputs to total solutes. PC2 explaining 15% of the total variance had strong positive loading on NH_4^+-N and moderate positive loading on TN, representing the nutrient component in waters. The third and fourth components together explained 23.6% of the total variance and were characterized by BOD and Cd, and turbidity and COD_{Mn}, respectively. PC3 represented organic and metal

pollutants primarily caused by industrial effluents, while domestic and industrial, and waste disposal for PC4.

Similar to September 2006, EC, TDS, Hard, and Cl^- in December 2006 and April 2007 were well correlated with PC1 and major pollutants were not included in the fist component. As regards December 2006, PC2 represented nutrient pollution, and the third and fourth components had higher loadings on BOD and COD_{Mn}, representing biodegradable and organic pollutants. PC5 explaining relatively lower variance (<9%) was dominated by the toxic metal-Cd, and thus indicating the influence of industrial wastes. While for April 2007, the second component explaining 18% of variance included nitrogen and organic pollutants with positive loadings on COD_{Mn} and BOD and a negative loading on Orp, thus this component pointed to organic pollution from anthropogenic activities. Further, high concentrations of biodegradable and organic pollutants in urban wastewater consumed large amounts of oxygen, leading to anaerobic fermentation processes and higher levels of ammonium and organic acids. Hydrolysis of these acidic materials thus decreased water pH values (Fig. 4) [4].

In contrasts to other three seasons, PC1 in June 2007 explained the total variance of 50% and included EC, TDS, COD_{Mn}, BOD, NH_4^+-N, Hard, Cl^-, SO_4^{2-}, Mn and Fe (Table 4), reflecting the mixes of anthropogenic and natural processes. PC2 explaining 24% of total variance had strong positive loadings on turbidity, TP, and moderate positive loadings on TSS, NH_4^+-N and HCO_3^-, and a negative loading on Orp. This also indicated alga blooming and anaerobic environment and therefore lower Orp. PC3 (9.3% of total variance) represented heavy metal pollution (Cd) by industrial effluents.

Overall, FA/PCA demonstrated great seasonality for water quality parameters, i.e., COD_{Mn}, BOD, NH_4^+-N, TN, TP and Cd, however, a few variables such as EC, TDS, Hard, Cl^- and Mn were always in PC1. This is consistent with the results that seasonal differences in concentrations are statistically significant shown in ANOVA test reported in Table 4. Moreover, the correlation coefficients between PCs and water quality parameters in Table 4 revealed the relative importance of a variable in a PC [8]. In this study, an absolute correlation coefficient value greater than 0.80 was considered to be an important variable influencing seasonal water quality. EC, TDS, Hard, Cl^- and Mn in PC1 were the most important variables contributing to water quality variability, reflecting natural processes and great impacts of salts by domestics and Cl-contained industry such as dyeing, pharmaceutical and pesticide on water quality. Major pollutants such as COD_{Mn}, BOD, NH_4^+-N, TN, TP and Cd had varying correlation coefficients with PCs, indicating seasonal heterogeneity in anthropogenic activities and hydro-climatic variability, i.e., precipitation and agriculture concentrating in summer and autumn, as well as daily differences of industrial effluents. Also, FA/PCA revealed four major groups of parameters: (1) EC, TDS, Hard, Cl^- and Mn (mainly natural), (2) toxic metals (industrial), (3) nutrients (agricultural and industrial) and (4) organic pollutants (domestic, municipal and industrial effluents). Three to five factors could explain 79%–88% of the total variance, thus, this statistical technique successfully deciphered possible pollution sources [3,4,7].

Hierarchical CA was employed to detect spatial similarity for sites and rendered a dendrogram grouping the sampling sites into three statistically significant clusters at (Dlink/Dmax) × 100 <65 (Fig. 5). Cluster 1 (sites 1–6, 8, 9, 11, 13, 16), cluster 2 (sites 7, 10, 12, 14, 15, 17 and 19) and cluster 3 (site 18) corresponded to moderated pollution, high pollution, and very high pollution regions, respectively (Fig. 5). This clustering was confirmed by the total factor scores (TFS) from FA versus sampling sites, reflecting their pollution levels [19], i.e., TFS for site 18 was the highest (1.6), and TFS with greater than 0 for sites 7, 10, 12, 14, 15, 17 and 19. Cluster 3 (site 18) with very high mineralization (4850 mg/l) was consistent

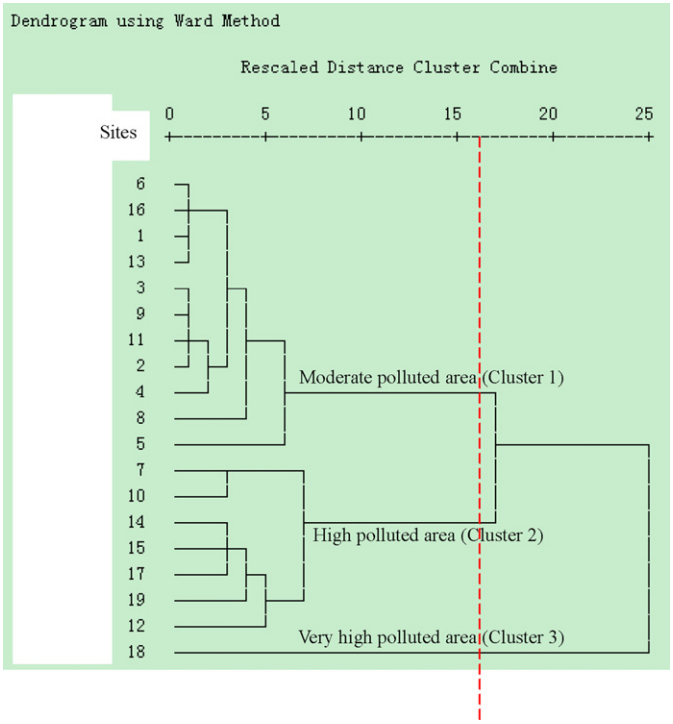

Fig. 5. Dendrogram showing clustering of sampling sites according to Ward's method using squared Euclidean distance.

with the fact that this river went through the Tianjin city and thus was polluted by urban's industrial and domestic wastes. ANOVA showed 75% of total variables with spatial significant variations (Table 6), indicating remarkably spatial heterogeneity in anthropogenic activities and economic development, i.e., agriculture in Henan and Hebei, while Beijing and Tianjin with developed economy and high dense population. Pollutants thus sourced from a combination of agricultural, industrial and domestic processes in Henan and Hebei provinces, while from industrial and domestic activities in Beijing and Tianjin, i.e., 60×10^4 t/yr of COD for Henan and Hebei, and about 10×10^4 t/yr of COD for Beijing and Tianjin, respectively (Fig. 2). The Haihe River near Beijing and Tianjin city is one of the most contaminated rivers in China [Fig. 5; [37]].

3.2. Source identification

Spatial heterogeneity of anthropogenic activities and economic development has resulted in diverse pollution source types in the region. In our work, precisely source identification/apportionment was calculated based on geographic characterization. Two categories were therefore obtained: (1) sites 1–14 in Henan and Hebei, where agriculture accounted for more than 50% of its respective GDP (gross domestic product), and (2) sites 15–19 in Beijing and Tianjin with little agricultural activities. We hypothesized that pollutants in group 1 were contributable to agricultural, industrial and domestic sources, while those in group 2 were industrial and domestic in origin.

Five PCs, with eigenvalue >1 and explaining 88% of the total variance, were extracted for sites in Henan and Hebei (group 1, Table 7). PC1 accounting for 29% of the total variance had strong loadings on Orp, EC, TDS, turbidity and TSS, and moderate positive loadings on NH_4^+-N, TN, Hard and HCO_3^-, indicating its association with dissolution of soil constituents mainly carbonates. Nitrogen variables and TSS were the primarily origins in run-off from fields with high load of soils and waste disposal activities. PC2 was heavily weighted

Table 6
Mean values with standard errors (S.E.) and ANOVA for water quality in different clusters of rivers along the canal system, China.

	Moderate polluted			High polluted			Very high polluted			ANOVA	df	Mean square	*F*	*p*-value
	n	Mean	S.E	*n*	Mean	S.E	*n*	Mean	S.E	Sum of squares				
T (°C)	105	16.94	0.86	70	18.77	1.14	10	19.13	3.15	160.28	2	80.14	0.95	0.388
EC (μs/cm)	105	622.86	26.51	70	1566.81	63.62	10	7459	820.61	432006720.32	2	216003360.16	447.60	0.000
TDS (mg/l)	105	406.97	17.52	70	1010.74	43.3	10	4850.1	533.11	182304291.41	2	91152145.70	436.75	0.000
pH	105	7.93	0.04	70	7.66	0.05	10	6.83	0.21	12.29	2	6.14	33.72	0.000
Orp (mV)	105	31.26	4.76	70	−76.08	15.03	10	−1.96	53.15	484819.71	2	242409.86	27.70	0.000
Turb (NTU)	105	12.25	1.62	70	51.51	7.56	10	41.06	14.53	66355.92	2	33177.96	18.66	0.000
TSS (mg/l)	65	21.34	3.68	59	155.86	35.47	9	84	12.32	559673.76	2	279836.88	8.32	0.000
COD_{Mn} (mg/l)	105	42.29	7.79	70	22.81	1.55	10	30.23	3.58	16114.46	2	8057.23	2.17	0.117
BOD (mg/l)	105	4.79	0.38	70	8.48	1.06	10	10.73	3.44	758.71	2	379.35	8.56	0.000
NH_4^+-N (mg/l)	105	1.29	0.48	70	11.54	2.2	10	14.78	4.05	5243.25	2	2621.63	17.46	0.000
TN (mg/l)	76	58.63	1.68	49	89.78	5.39	7	62.98	9.26	29328.58	2	14664.29	21.48	0.000
TP (mg/l)	67	0.6	0.12	63	0.73	0.1	7	0.57	0.09	0.65	2	0.32	0.40	0.674
Hard (mmol/l)	105	2.97	0.11	70	5.15	0.12	10	14.5	1.79	1271.45	2	635.73	241.77	0.000
Cl^- (mg/l)	105	42.38	3.82	70	204.58	16.55	10	1015.74	31.43	8912211.72	2	4456105.86	516.08	0.000
SO_4^{2-} (mg/l)	104	84.20	6.68	64	141.38	11.00	10	313.19	122.63	534791.36	2	267395.68	20.17	0.000
HCO_3^- (mg/l)	105	212.53	8.09	70	448.52	14.23	10	117.46	16.03	2678623.41	2	1339311.70	142.06	0.000
Cu (mg/l)	35	0.09	0.01	44	0.09	0.01	8	0.1	0.03	0.00	2	0.00	0.02	0.978
Zn (mg/l)	68	0.06	0.01	49	0.06	0.01	10	0.06	0.01	0.00	2	0.00	0.00	0.997
Cd (mg/l)	91	0.02	0	69	0.02	0	10	0.04	0	0.00	2	0.00	11.93	0.000
Mn (mg/l)	93	0.08	0.01	69	0.1	0.01	10	0.84	0.21	5.24	2	2.62	92.45	0.000
Fe (mg/l)	67	0.09	0.01	50	0.13	0.02	6	0.36	0.1	0.40	2	0.20	11.41	0.000

in BOD, NH_4^+-N, TN and SO_4^{2-}. Nitrogen fertilizers were widely used in Henan and Hebei provinces (China's major grain production base), thus agricultural runoff could be dominantly responsible this PC, whereas, SO_4^{2-} was primarily contributable to fossil fuel combustion for thermal power and acid rain in this region. The third and fourth PCs together explaining 29% of total variance were most dependent upon COD_{Mn}, Cl^-, Cu, Mn, Cd, TP and Zn, representing heavy metal contamination, organic and reductive pollutants. This cluster was primarily due to industrial processes such as metallurgy, petrochemical plants, chemical fertilizer and pesticides etc. However, domestics were also largely contributed to COD_{Mn} and Cl^- (salts). The last PC was interpreted as natural processes because of high loading on Hard (Ca and Mg) and Fe, and these elements were found abundant in earth crust.

Three PCs explaining 80% of the total variance were extracted from the rivers in Beijing and Tianjin (group 2, Table 7). The first PC included more than half variables and explained 42% of total variance. These variables represented solutes, ammonium, major elements (Hard, Cl^- and HCO_3^-), and heavy metals, thus, PC1 indicated the combinations of natural and anthropogenic sources. PC2 was well correlated with turbidity, COD_{Mn}, BOD, SO_4^{2-} and Cu and contributed 21.5% to total variance. 90% COD_{Mn} in Beijing and 80% COD_{Mn} in Tianjin sourced from domestics (Fig. 2), hence, we mainly ascribed this PC to domestics. Coal combustion (primarily coal-fire power plants, thermal power industry, and heating of buildings in winter) and motor vehicle exhaust partially contributed to SO_4^{2-} and Cu. This is consistent with the fact that high pollution levels of atmospheric sulfur oxide occur in winter and spring in North China, i.e., SO_2 in Beijing increased from 10 ppb in summer to 46 ppb in winter with the highest value of 113 ppb [46,47]. PC3 (16% of total variance) had strong positive loadings on TN and TP, representing nutrient pollution. Excess nutrients led to eutrophication and

Table 7
Varimax rotated factor loading and corresponding possible source type (the significance of KMO and Bartlett's sphericity test is <0.001).

Sites 1–14	Component					Communality	Sites 15–19	Component			Communality
	1	2	3	4	5			1	2	3	
Orp	**−0.79**	−0.44	0.06	−0.08	−0.20	0.88	Orp	−0.21	−0.31	**−0.82**	0.81
EC	**0.83**	0.21	0.31	0.04	0.35	0.96	EC	**0.97**	0.00	0.08	0.95
TDS	**0.83**	0.20	0.17	−0.04	0.26	0.82	TDS	**0.97**	0.00	0.08	0.95
Turbidity	**0.79**	0.50	−0.07	0.11	0.09	0.90	Turbidity	−0.08	**−0.82**	−0.10	0.68
TSS	**0.91**	−0.02	−0.07	0.17	−0.16	0.89					
COD_{Mn}	0.35	0.29	**0.65**	0.21	0.46	0.88	COD_{Mn}	0.21	**−0.69**	−0.18	0.55
BOD	0.35	**0.84**	−0.18	0.13	−0.15	0.90	BOD	−0.14	**0.83**	0.04	0.70
NH_4^+-N	0.59	**0.72**	−0.24	0.06	0.11	0.95	NH_4^+-N	**0.95**	0.00	0.08	0.90
TN	0.58	**0.77**	−0.12	−0.01	0.11	0.95	TN	−0.04	0.23	**0.92**	0.90
TP	−0.32	−0.35	−0.10	**−0.80**	0.05	0.88	TP	−0.04	0.06	**0.95**	0.91
Hard	0.60	0.00	0.30	0.14	**0.65**	0.88	Hard	**0.97**	0.05	0.03	0.95
Cl^-	0.38	−0.15	**0.81**	0.01	0.22	0.88	Cl^-	**0.93**	0.06	0.03	0.88
SO_4^{2-}	0.04	**−0.84**	−0.35	0.05	−0.16	0.86	SO_4^{2-}	0.35	**0.77**	0.26	0.78
HCO_3^-	**0.70**	**0.59**	0.22	0.11	0.29	0.98	HCO_3^-	**−0.76**	−0.38	0.47	0.94
Cu	−0.01	0.16	**−0.66**	0.58	−0.27	0.86	Cu	0.14	**0.85**	0.09	0.74
Zn	0.03	0.13	0.34	**−0.79**	−0.02	0.77	Zn	**0.79**	−0.23	−0.08	0.68
Mn	−0.11	−0.05	**0.86**	−0.20	−0.10	0.81	Mn	**0.72**	0.02	−0.05	0.52
Cd	0.14	−0.25	**−0.70**	0.53	0.12	0.87	Cd	**0.73**	0.42	0.13	0.73
Fe	0.13	0.09	−0.01	−0.13	**0.93**	0.91					
Eigenvalue	8.29	4.12	2.01	1.26	1.12		Eigenvalue	7.31	4.10	2.18	
Cumulative %	29.13	48.80	66.57	77.63	88.45		Cumulative %	41.90	63.47	79.94	

Possible sources type: Sites 1–14, PC1, Natural (primarily) + anthropogenic; PC2, Agricultural + fossil fuel; PCs 3 and 4, Industrial + domestic; PC5, Natural. Sites 15–19, PC1, Natural + anthropogenic (primarily); PC2, Domestic 1 + industrial 1 (coal combustion, vehicle); PC3, Domestic 2 (detergent, faeces) + industrial 2 (petroleum refining).

Table 8
Source contribution (in %) to elements calculated using FA-MLR technique.

Sites 1–14	F1	F2	F3	F4	F5	R^2	Sites 15–19	F1	F2	F3	R^2
Orp	50.05	27.81	4.08	5.23	12.84	0.84	Orp	15.44	23.06	61.50	0.77
EC	48.06	12.01	17.71	2.32	19.90	0.94	EC	91.87	0.46	7.67	0.94
TDS	55.22	13.40	11.69	2.37	17.32	0.77	TDS	91.71	0.43	7.86	0.95
Turbidity	50.85	31.86	4.50	7.26	5.54	0.87	Turbidity	8.44	81.58	9.98	0.63
TSS	68.12	1.52	5.61	13.00	11.75	0.86					
COD_{Mn}	17.78	14.76	33.31	10.65	23.50	0.84	COD_{Mn}	19.67	63.71	16.62	0.49
BOD	21.08	51.27	10.89	7.77	8.99	0.87	BOD	41.74	46.79	11.46	0.65
NH_4^+-N	34.51	41.98	13.71	3.62	6.18	0.93	NH_4^+-N	91.52	0.37	8.11	0.89
TN	36.47	48.64	7.51	0.36	7.02	0.93	TN	2.98	19.56	77.46	0.88
TP	19.51	21.44	6.38	49.37	3.30	0.84	TP	4.21	5.46	90.33	0.89
Hard	35.46	0.03	17.74	8.30	38.48	0.84	Hard	92.16	5.11	2.73	0.94
Cl^-	23.95	9.72	51.55	0.58	14.20	0.84	Cl^-	90.68	6.30	3.01	0.85
SO_4^{2-}	2.99	58.31	24.23	3.57	10.90	0.81	SO_4^{2-}	25.35	55.59	19.06	0.74
HCO_3^-	36.79	30.86	11.66	5.62	15.07	0.97	HCO_3^-	54.33	8.69	36.98	0.94
Cu	0.77	9.51	39.22	34.59	15.91	0.82	Cu	12.89	79.06	8.05	0.69
Zn	2.27	9.67	26.09	60.69	1.27	0.70	Zn	71.33	21.18	7.49	0.62
Mn	8.56	3.47	65.44	15.09	7.44	0.81	Mn	91.65	2.45	5.90	044
Cd	8.24	14.07	40.05	30.58	7.06	0.84	Cd	56.87	33.00	10.12	0.68
Fe	10.25	7.10	0.79	9.88	71.98	0.89					

Possible sources type: Sites 1–14, F1, Natural (primarily) + anthropogenic; F2, Agricultural + fossil fuel; F3 and F4, Industrial + domestic; F5, Natural. Sites 15-19, F1, Natural + anthropogenic (primarily); F2, Domestic 1 + industrial 1 (coal combustion, vehicle); F3, Domestic 2 (detergent, faeces) + industrial 2 (petroleum refining).

alga bloom, hence anaerobic environment, thus this PC had strong negative loading on Orp.

3.3. Source apportionment

Using the PCA results above, FA-MLR receptor modeling was applied to quantify the source contributions to each measured water quality variables (Table 8). It is worth noting that for each individual factor containing mixed sources, the tracer for a source was assumed to be exclusively emitted from that specific source. High R^2 listed in Table 8 and the ratio of mean calculated to measured values around one suggested goodness of the receptor model on source apportionment.

For group 1 (rivers in Henan and Hebei), the model showed that the first factor was dominantly controlled by natural processes (e.g., soil weathering) which contributed 50% to solute load, while the fifth factor (purely earth crust source) contributed 17% to river solutes, resulting in 67% of solutes apportioned to natural processes. Over 50% of nitrogen was attributable to agriculture, which was consistent with the fact of intense agricultural activities in these two provinces. Industrial and domestic sources contributed 70% of heavy metals and more than a half of COD_{Mn}, phosphorus and Cl^-.

The first factor for the group 2 (rivers in Beijing and Tianjin) represented multiple sources due to that the major pollutants such as ammonium and toxic metals were primarily contributed by this factor, resulting smaller proportion of natural sources to riverine solutes. Domestic sources contributed 64% of COD_{Mn} and 47% of BOD, while SO_4^{2-} (56%) was predominantly attributable to coal combustion and vehicle exhaust. The last factor was largely dominated by industrial effluents, contributing 77% of nitrogen and 90% of phosphorus, though some domestic sources such as detergent and faeces also contributed to them. Considering COD_{Mn} partially attributed to domestic source of factor 3, COD_{Mn} from domestics was high as 80%, which was close to the results obtained from emission inventory (80–90%) in Beijing and Tianjin city (Fig. 2) [37].

4. Conclusion

There are considerably spatio-temporal variabilities in water quality in the rivers along the water conveyance system of the Middle Route of the South to North Water Transfer Project. Rivers northward were more polluted by industrial effluents. Hierarchical cluster analysis in combination with total factor scores versus sampling sites grouped the sampling sites into three clusters of similar characteristics between sampling sites corresponding to moderate, high and very high polluted rivers. Seasonal FA/PCA allowed four categories of parameters such as mineral composition (primarily natural), toxic metals (industrial), nutrients (agricultural, domestic and industrial) and organic pollutants (domestic, municipal and industrial sources).

Multi-linear regression with factor analysis (FA-MLR) receptor modeling provided apportionment of various sources contributing to river pollution. For rivers in Henan and Hebei provinces, industrial and domestic sources contributed 70% of heavy metals and more than half of COD_{Mn}, phosphorus, and Cl^-, while 50% of nitrogen from agriculture. Industrial effluents were the major sources for nitrogen and phosphorous, and domestics contributed 80% to COD_{Mn} for rivers in Beijing and Tianjin. Clean techniques in industry and reduction of agricultural runoffs should be adopted to minimize pollutants to rivers. This study demonstrated usefulness of multivariate statistic techniques in water quality assessment, source identification/apportionment, which would help obtain better information on the water quality for water conservation.

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