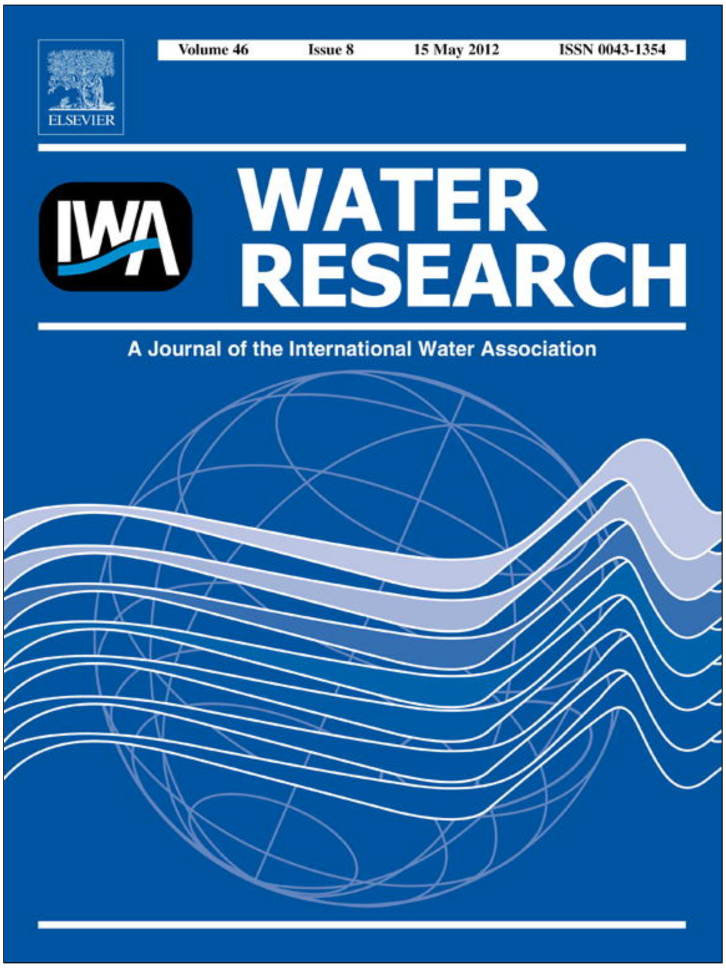
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Hydrochemical characteristics and water quality assessment of surface water and groundwater in Songnen plain, Northeast China

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ABSTRACT

Water quality is the critical factor that influence on human health and quantity and quality of grain production in semi-humid and semi-arid area. Songnen plain is one of the grain bases in China, as well as one of the three major distribution regions of soda saline-alkali soil in the world. To assess the water quality, surface water and groundwater were sampled and analyzed by fuzzy membership analysis and multivariate statistics. The surface water were gather into class I, IV and V, while groundwater were grouped as class I, II, III and V by fuzzy membership analysis. The water samples were grouped into four categories according to irrigation water quality assessment diagrams of USDA. Most water samples distributed in category C1-S1, C2-S2 and C3-S3. Three groups were generated from hierarchical cluster analysis. Four principal components were extracted from principal component analysis. The indicators to water quality assessment were Na, HCO_3, NO_3, Fe, Mn and EC from principal component analysis. We conclude that surface water and shallow groundwater are suitable for irrigation, the reservoir and deep groundwater in upstream are the resources for drinking. The water for drinking should remove of the naturally occurring ions of Fe and Mn. The control of sodium and salinity hazard is required for irrigation. The integrated management of surface water and groundwater for drinking and irrigation is to solve the water issues.

1. Introduction

Water is the key resource for human living, especially for drinking and irrigation. Water quality is very important to human healthy and the quantity and quality of grains by effecting on soils, crops and environment (Hoek et al., 2001; Kirda, 1997). The water quality assessment is mostly based on hydrochemical analysis. World Health Organization (WHO) published the guidelines for drinking water to protect public health. The concentrations of naturally occurring chemicals, such as chloride, iron, manganese, sodium etc. are not of health concern at levels, but may affect acceptability of drinking water. The guideline value for chemical from agricultural activities, such as nitrate, is less than 50 mg/L (World

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Health Organization, 2011). The guidelines of water quality for agriculture is provide by the Food and Agriculture Organization of the United Nations (FAO) (Ayers and Westcot, 1985). The water quality for irrigation may effect the soils and crops, especially in the saline alkali soil areas. Salinity and sodium hazard indicators can be used as a criterion to find the suitability of irrigation waters (Nishanthiny et al., 2010). The USDA (United States Department of Agriculture) method is the most recognized worldwide, and sodium absorption ratio (SAR) is an effective evaluation index for most irrigation water (Al-Bassam and Al-Rumikhani, 2003; Ayers and Westcot, 1985; Richards, 1954). Elevated values of SAR result in decreased hydraulic conductivity, decreased aggregate stability, clay dispersion, swelling of expandable clays, surface crusting and reduced tillage (Suarez et al., 2006). The quality standards for surface water, groundwater, drinking water and irrigation water have been published (General administration of quality supervision inspection and quarantine of the people's republic of China, 1993, 2006; Ministry of environmental protection of the people's republic of China, 2002; Ministry of health of the people's republic of China, 2006). The guideline values of these standards are stricter than the values of WHO and FAO.

Water quality management are characterized by imprecision in objectives and water quality standards. However, fuzzy mathematics provide a useful technique in addressing such imprecision (Mujumdar and Sasikumar, 2002; Saruwatari and Yomota, 1995; Saslkumart and Mulumdart, 2000). Moreover, multivariate statistics techniques are the efficient method to analyze the water samples and characteristics of hydrochemistry (Singh et al., 2004). Hierarchical cluster analysis (HCA) is a powerful tool for analyzing water chemical data. It can be used to test water quality data and determine if samples can be grouped into distinct populations (hydrochemical groups) that may be significant in the geologic/hydrologic context, as well as from a statistical point of view. Principal components analysis (PCA) was useful for data reduction, to assess the continuity/overlap of clusters or clustering/similarities in the data, and was used to determine the sources of variation between parameters (Güler et al., 2002).

The Songnen plain is one of the main bases for grain production and animal husbandry in the northeastern China (Wang et al., 2004). It is one of the three major distribution regions of soda saline-alkali soil in the world (Zhang et al., 2007). Songnen plain was development relatively late, only about 100 years in the temperate zone of the world. The grain production increased significantly after 1995, especially the increasing of rice output (Fig. 1(a)). At the same time, the groundwater irrigation area increased rapidly with the rice production increase. (Fig. 1(b)). Groundwater with high salinity has been widely abstracted from the unconfined aquifer for irrigation in the dry land by local farmers due to water shortage and expenditure problems. As a result, a large area of secondary saline–alkaline land has been induced and the slightly saline–alkaline land has been aggravated (Zhang et al., 2007). The surface water and groundwater resources are not only used as irrigation water to grain production, but also the drinking water for the millions people. The water quality for drinking and irrigation and the water quality management are the most concern issues under the rapidly industrial and agricultural development in Songnen plain.

The water samples were sampled and analyzed in this study to character the hydrochemical characteristics of the surface water and groundwater, and assess the water quality by fuzzy membership according to the china national standards for surface water, groundwater, drinking water and irrigation water. The salinity diagram of USDA was also used to evaluate the water quality for irrigation. Hierarchical cluster analysis (HCA) was used to classify the water samples into different groups based on chemical parameters. Principal component analysis (PCA) was used to reduce the chemical parameters in order to assess water quality by comprehensive chemical variables. The conclusions were drawn for improving water management and increasing the availability of good quality water for sustainable development.

2. Study area

The Songnen plain (121°27′–128°12′ E, 43°36′–49°45′ N) is an alluvial, lacustrine and aeolian deposit that developed on the base of a faulted basin in the Mesozoic, locating in the central part of Northeast China (Fig. 2). The plain is with the boundaries of Changbai Mountains in the east, Daxingan (Greater Khingan) Mountains in the west, Xiaoxingan (Leesser Khingan) Mountains in the north and Songliao watershed divide in the south. The total area is 1.87×10^5 km^2, including Heilongjiang Province and Jilin Province in district. The main cities in the area are Haerbin, Changchun, Qiqihaer, Daqing, and Baicheng, etc. The total population of the area is 32.31 million in 2003 (Xiao et al., 2009).

The climate of Songnen plain is temperature semi-humid and semi-arid continental monsoon climate. The mean annual precipitation is 350–600 mm, with 70–80% of precipitation occurring in June to September. The average annual temperature is 4.0–5.5 °C. The average temperature is −16∼−26 °C in January, while the average temperature is 21–23 °C in July. The evaporation from water surface is 700–1100 mm. The Songnen plain belongs to the drainage of Songhua River. The second Songhua River and Nen River merge in the center of the area, and then compose Songhua River. The discharge rate of Songhua River is 40.8 billion m^3/a at the Haerbin station. (Xiao et al., 2009).

The main types of soils include black soil, chernozem, meadow soil, swamp soil, halic soil, sandy soil, and paddy soil. The typical zonal soils are black soil and chernozem. The halic soils are mainly distributed in the western part of the plain. The area of saline-alkalization land amounted to only 2.4×10^6 ha in the 1950s, but it had reached to 3.20×10^6 ha at the beginning of the 1990s, and it is still increasing at a rate of 2×10^4 ha/a (Wang et al., 2004). The grasslands are mainly distributed in the west of the Songnen plain and interlaced with farmland. The landscape vegetation is *Leymus chinesis* meadow in the area (Li and Zhou, 2001). The majority of upland crops are wheat, corn and soybean. The crop-growing season is generally from May to September. The average grain yields of rice, wheat, corn and soybean over the period 1978–2008 were 5.23, 2.81, 4.36 and 1.82 t/ha, respectively.

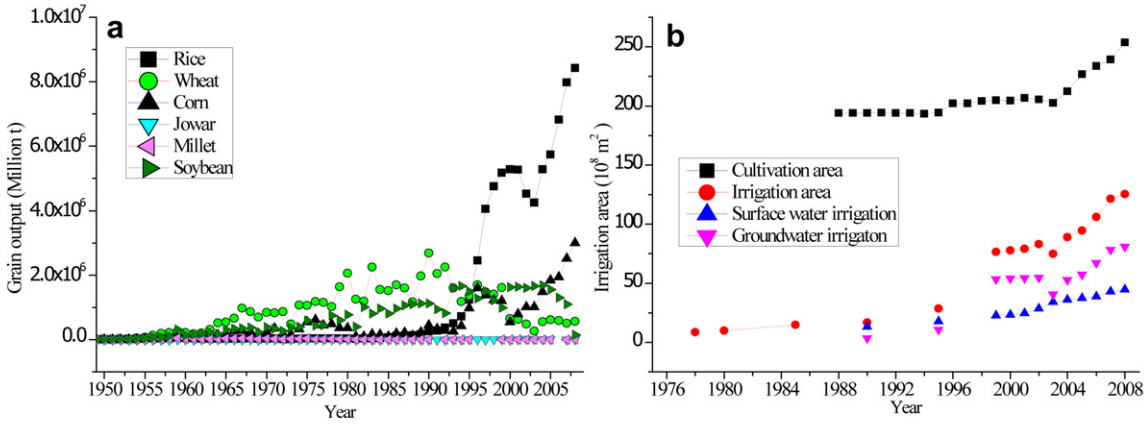

Fig. 1 – The increase of grain production from 1950 to 2008 (a) and area of cultivation and irrigation from 1970s to 2008 (b). Data from the Statistical yearbook of Heilongjiang reclamation area (Heilongjiang land reclamation bureau, 2009).

3. Methods

3.1. *Water sampling*

Surface water and groundwater were sampled along Songhua River, the second Songhua River and Nen River for major ions analysis during August 2010 (Fig. 2). The surface water was sampled in rivers, lakes, reservoirs. The irrigation water in the paddy field was sampled at the Da'an sodic land ecology experiment station. The wetland water was collected at the Zhalong nature preserve. Shallow and deep groundwater samples were collected from shallow (sampling depth <60 m) and deep (sampling depth > 60 m) wells. Two 50 ml polyethylene bottles with watertight caps were used to store filtered (0.45 μm Millipore membrane filter) water for cations and anions analysis. One bottle was acidified with HCl to pH ~ 2 for cations determination. The other bottle for anions analysis was kept unacidified. All samples were stored at 4 °C after bottling.

3.2. *Analytical techniques*

Electrical conductivity (EC), pH, water temperature (Tem) and total dissolved solids (TDS) were measured in situ via an EC/pH meter (WM22EP, Toadkk, Japan), which was previously calibrated. The HCO_3 concentration was determined by titration with 0.02 N sulfuric acid on the day of sampling before filtration, methyl orange endpoint titration was used with the final pH being 4.2–4.4 (Zhang et al., 2010).

The major ions of water samples were treated and analyzed in the physical and chemical analysis center laboratory of the Institute of Geographic Sciences and Natural Resources Research (IGSNRR), Chinese Academy of Sciences (CAS). Cations (Na, K, Ca, Mg, Fe and Mn) analysis of water samples were measured by inductively coupled plasma optical emission spectrometry (ICP-OES) (Perkin–Elmer Optima 5300 DV, USA). Major anions (Cl, NO_3, and SO_4) were carried out on ion chromatography (IC) (Shimadzu LC-10ADvp, Japan). The limits of detection of ICP-OES and IC are 1 μg/L and 1 mg/L, respectively. Analytical precision for major ions was within 1%. For all water samples, ion balance errors (IBE) were <10%, and most of them were <5%.

3.3. *Water quality indices*

Excessive sodium and salinity concentrations in irrigation water result in sodium hazard, as well as salinity hazard. Sodium ion in water replacing calcium and magnesium ions in soil causes reduced permeability and soil harden (Shaki and Adeloye, 2006). To assess irrigation water quality, the parameters such as percent sodium (Na%) and sodium adsorption ratio (SAR) were calculated based on the chemical variables of water samples (Singh et al., 2005). The irrigation water assessment indices including:

$$\text{percantage sodium,}\quad \text{Na\%} = \frac{\text{Na}^+}{\text{Na}^+ + \text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^+} \times 100\% \tag{1}$$

$$\text{sodium adsorption ratio,}\quad \text{SAR} = \text{Na}^+ / \sqrt{(\text{Ca}^{2+} + \text{Mg}^{2+})/2} \tag{2}$$

where all the ionic concentrations are expressed in milliequivalents per liter (meq/L) of the respective ions. The SAR is probably the only one in current use and is generally considered an effective evaluation index for most water used in irrigated agriculture (Ayers and Westcot, 1985).

3.4. *Fuzzy membership function*

Water quality management is characterized by imprecision in objectives and water quality standards. Fuzzy sets and fuzzy optimization provide a useful technique in addressing such imprecision (Mujumdar and Sasikumar, 2002).The fuzzy membership function was used to assess water quality according to the standards. To reduce the complexity of the model, the linear membership functions are used. This membership function is expressed as

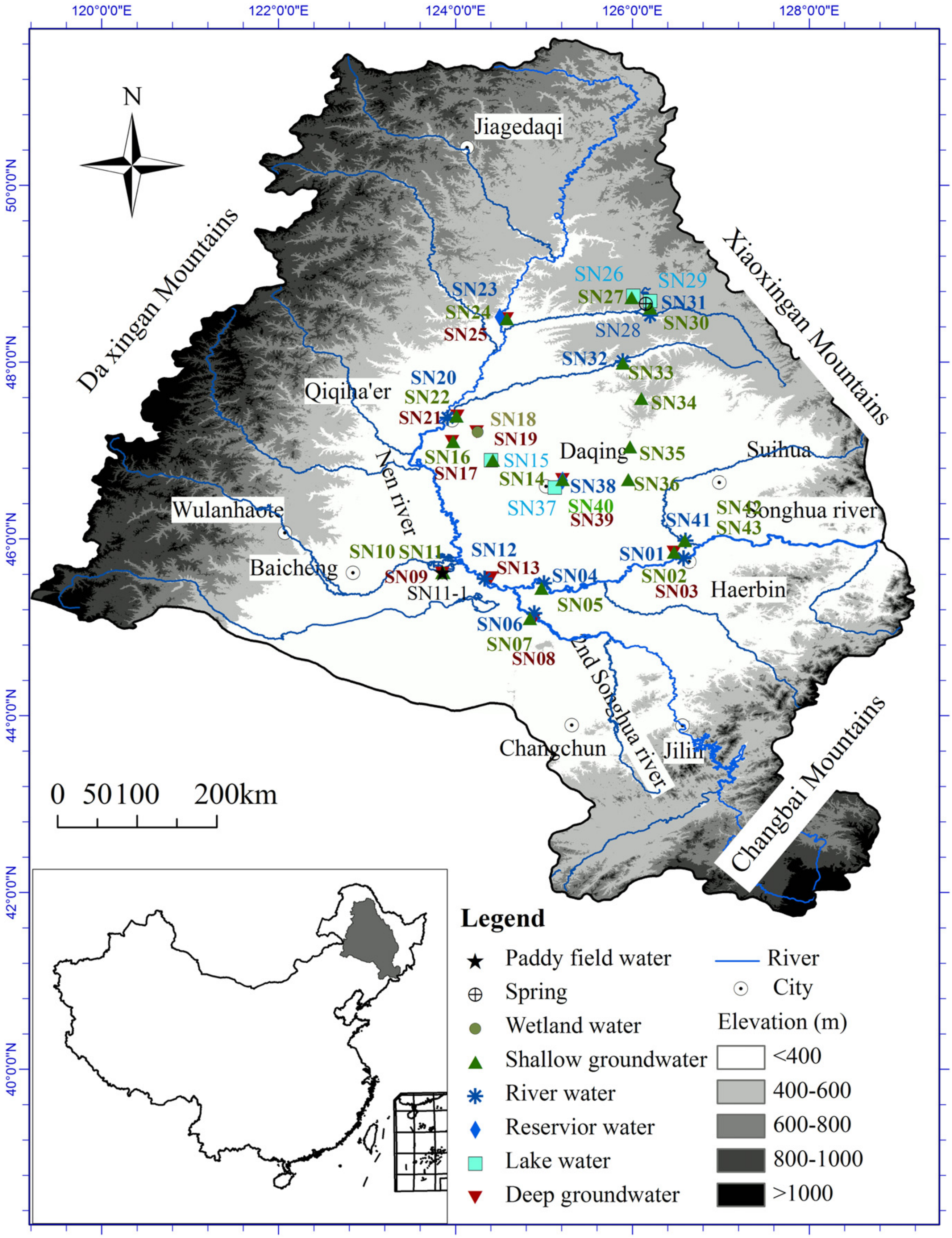

Fig. 2 – The location of Songnen plain and distribution of water samples.

$$r_{ij} = \begin{cases} 0, (C_i \le S_{ij-1} \text{ or } C_i \ge S_{ij-1}) \\ \dfrac{C_i - S_{ij-1}}{Si_j - S_{ij-1}}, \ (S_{ij-1} < C_i < S_{ij}) \\ \dfrac{S_{ij+1} - C_i}{Si_{j+1} - Si_j}, \ (S_{ij} < C_i < S_{ij+1}) \\ 1, (C_i = S_i) \end{cases} \tag{3}$$

where r_{ij} indicates the fuzzy membership of indicator i to class j, C_i stands for analytical value of water quality indicator i, S_{ij} stands for the allowable value of water quality indicator. The fuzzy membership matrix R consists of water quality indicators and classes.

The weight of water quality indicator is expressed as

$$W_i = \frac{C_i}{S_i} \tag{4}$$

where W_i is the weight of water quality indicator i, C_i is the analytical value of water quality indicator i, S_i is the arithmetic mean of allowable values of each class. The normalized weight of each indicator is calculated by the formula

$$a_i = \frac{C_i}{S_i} / \sum_{i=1}^{m} \frac{C_i}{S_i} = W_i / \sum_{i=1}^{n} W_i \tag{5}$$

where a_i is the normalized weight of indicator i, $\sum_{i=1}^{n} W_i$ is the sum of weight to all water quality indicators. The fuzzy A consists of weight of each water quality indicator.

The water quality assessment by fuzzy membership is based on the matrix B,

$$B = A \cdot R \tag{6}$$

The fuzzy B is the matrix of membership to each water quality class. Water sample is classified to the class with the maximize membership.

3.5. *Statistical analysis*

Water samples were classified by water quality assessment indices, including percent sodium and sodium absorption ratio. To compare the water groups, the most efficient grouping method statistical clustering techniques were achieved. Hierarchical cluster analysis (HCA) was used in this study to group water samples into significant groups based on all the chemical parameter (variables). Principal components analysis (PCA) was useful for data reduction, to assess the continuity/overlap of clusters or clustering/similarities in the data, and was used to determine the sources of variation between parameters (Güler et al., 2002). In the PCA, varimax rotation was applied to the principal components in order to find factors that can be more easily explained in terms of hydrochemical or anthropogenic processes. The SPSS® release 16.0 (SPSS Inc, Chicago, USA) was used to analyze the hydrochemical data. The statistical analysis of HCA and PCA were carried out via the classify and data reduction modules, respectively.

4. Results

4.1. *Hydrochemical characteristics*

The hydrochemical characteristics of surface water and groundwater are showed in Table 1 by descriptive statistics method. The major cations of surface water and groundwater dominated with Na and Ca, while the major anions dominated with HCO_3 and Cl. The standard deviation of electronic conductivity is the largest in both surface water and groundwater. The standard deviation of manganese and iron concentration is the least in surface water and groundwater, respectively. The coefficient variation of sodium and manganese concentration is the largest in surface water and groundwater, respectively. The major cations and anions of surface water contribute 39.39% and 60.61% of total dissolved solids, respectively. However, the major cations and anions of groundwater contribute 35.22% and 64.78% of TDS, respectively.

The concentrations of calcium and magnesium in groundwater were larger than surface water, however, the

Table 1 – Descriptive statistics of surface water and groundwater hydrochemistry.

Item	Surface water					Ground water				
	Mean	Min	Max	S.D	CV (%)	Mean	Min	Max	S.D	CV (%)
Ca	18.48	3.61	34.67	7.67	41.53	61.06	3.41	242.30	50.09	82.03
Mg	7.47	1.22	22.00	6.48	86.73	17.92	0.49	68.78	14.72	82.17
Na	87.30	1.61	619.10	198.38	227.25	69.91	3.45	490.40	100.09	143.18
K	3.75	0.39	12.51	2.93	78.12	3.16	0.39	34.80	6.47	204.99
HCO_3	207.46	18.92	1120.00	365.27	176.06	244.78	42.10	1009.00	209.76	85.69
SO_4	19.98	1.44	102.30	25.02	125.24	35.92	0.48	135.50	37.13	103.37
Cl	54.32	1.06	314.50	88.35	162.67	85.80	1.42	412.70	102.19	119.10
NO_3	1.98	–	7.44	2.38	119.99	35.52	–	412.30	87.35	245.90
Fe	0.73	–	2.67	0.86	117.53	0.03	–	0.27	0.07	264.14
Mn	0.11	–	0.53	0.17	151.20	0.14	–	2.54	0.49	347.65
EC	501.96	43.90	2830.00	856.61	170.65	721.03	96.80	2680.00	583.68	80.95
pH	7.93	7.09	9.37	0.61	7.68	7.21	6.72	8.80	0.40	5.56
Tem	21.35	18.10	24.30	1.99	9.30	9.58	5.30	16.40	3.16	33.01

Units: Ion concentration (mg/L), TDS (mg/L), pH (standard units), EC (μS/cm), Tem. (°C), - below the limit of detection. S.D indicates standard deviation, CV indicates coefficient variation.

concentrations of sodium and potassium in groundwater were less than surface water. The concentrations of major anions in groundwater were larger than surface water. The mean values of iron and pH of surface water were larger than groundwater, while the values of manganese and electrical conductivity of groundwater were larger than surface water. The temperature of surface water was significantly larger than groundwater. The minimum temperature value of surface water was larger than maximum value of groundwater.

The major ions concentrations of surface water along the river flow direction, including river water, lake water, reservoir water and wetland water are showed as hexa-diagram in Fig. 3. The ions concentration and EC of river water were the least in upstream of Nen river. The major ions concentration and EC increased along river flow direction, but decreased after flowing through the middle of Songnen plain. The ions concentration and EC values of 2nd Songhua river water decreased after conjoin with Nen river. The lake waters in the middle of plain were more concentrated than the mountain area. The wetland water was also concentrated comparing to river water. The ions concentration and EC of reservoir water in upstream were less than the reservoir in the plain.

4.2. *Water quality assessment by fuzzy membership*

Fuzzy membership was used to assess surface water and groundwater quality according to the quality standards (Table 2). The evaluation parameters were concentrations of Cl, SO_4, NO_3, Fe, Mn, total dissolved solids and hardness. Surface water and groundwater were assessed into five classes for drinking and irrigation.

The river water was grouped into three classes. The number of samples within the class I, IV and V accounts for 37.5%, 50% and 12.5% of river water, respectively. Lake water samples were classified into the II and IV classes. Reservoir water and wetland water were excellent and were classified into the class I. Shallow groundwater samples were grouped into I, II, III and V classes, accounting for 57.9%, 10.5%, 26.3% and 5.3%, respectively. Deep groundwater was classified into classes I and II, accounting for 88.9% and 11.1%, respectively. The percentage of class I, II, III, IV and V of water samples were 62.8%, 7.0%, 11.6%, 14.0%, and 4.6%. Water qualities of most samples were good according to the assessment by fuzzy membership.

4.3. *Irrigation water quality*

The parameters such as electrical conductivity, sodium adsorption ratio (SAR), and percent sodium (Na%) were estimated to assess the suitability of surface water and groundwater for irrigation purpose. The irrigation waters classification diagrams were used to assess the water quality (Richards, 1954; Wilcox, 1955) (Fig. 4).

The river water, reservoir water and two lake waters fall in the category C1-S1 (Fig. 4(a)). Seven deep and eight shallow groundwaters fall in the category C2-S1.Six shallow groundwater and one deep groundwater fall in the category C3-S1. The deep groundwater sample (SN39) falls in the C2-S4 with very high sodium hazard. The lake water (SN15, SN37) fall in the category C4-S4 with very high sodium and salinity hazard. The shallow groundwater SN11, which was sampled in the Da'an sodic land ecology experiment station, distributes in the category C4-S3 with very high salinity and high sodium hazard. The shallow groundwater sample SN36 and the paddy field water (SN11-1) fall in C3-S2, with high salinity and medium sodium hazard.

The water samples were grouped into four categories according to irrigation water assessment with percent sodium and electrical conductivity (Fig. 4(b)). The category of excellent to good for irrigation consists of all river water, reservoir water, two lake water, ten shallow and seven deep groundwater samples. Five shallow and one deep groundwaters were grouped as good to permissible category. The shallow groundwater SN36 and the paddy field water fall in the category of permissible to doubtful. The deep groundwater (SN39), lake water (SN15, SN37), and shallow groundwater (SN11, SN40) were classified as doubtful to unsuitable for irrigation.

4.4. *Hierarchical cluster analysis*

Hierarchical cluster analysis (HCA) is used to test water quality data and determine if samples can be grouped into hydrochemical groups. The hierarchical cluster analysis method was used to group water samples into significant different clusters.

Three groups were generated from hierarchical cluster analysis (Fig. 5). Most of water samples were classified as group I, which including all river water, reservoir water, wetland water, two lake water, 12 shallow and eight deep groundwater samples. Group II consists of two subgroups. Subgroup 1 includes three shallow and one deep groundwater, while subgroup 2 includes the paddy field water and shallow groundwater SN36. Group III also consists of two subgroups. Subgroup 3 includes shallow groundwater SN11 and lake water SN15, while the subgroup 4 includes shallow groundwater SN40 and lake water SN37.

To compare the hydrochemistry difference of three clusters, the mean water chemistry is showed in Table 3. The ions concentrations and hydrochemical parameters of group III were the largest, except K, Fe, Mn and temperature. The ions concentrations of Fe, Mn and water temperature of group II were the least, however, the ion concentration of Mn in group I was the largest. The group I was assessed as class II by fuzzy membership. The group II and III, subgroup 1 and subgroup 4 were in class III, however, the subgroup 2 and subgroup 3 were classified as class III and IV, respectively.

4.5. *Principal component analysis*

Principal components analysis is a multivariate data analytic technique. It reduces a large number of variables to a small number of variables, without sacrificing too much of the information. The PCA was used to reduce water chemical parameters (variables). The PCA component matrix and rotated component matrix are showed in Table 4.

Four components were extracted from principal component analysis method. The cumulative variance explained by the four components was 80.99%. The PC1, PC2, PC3 and PC4 explains 28.41%, 28.22%, 14.76% and 9.6% of the total variance, respectively. The first component was correlated with

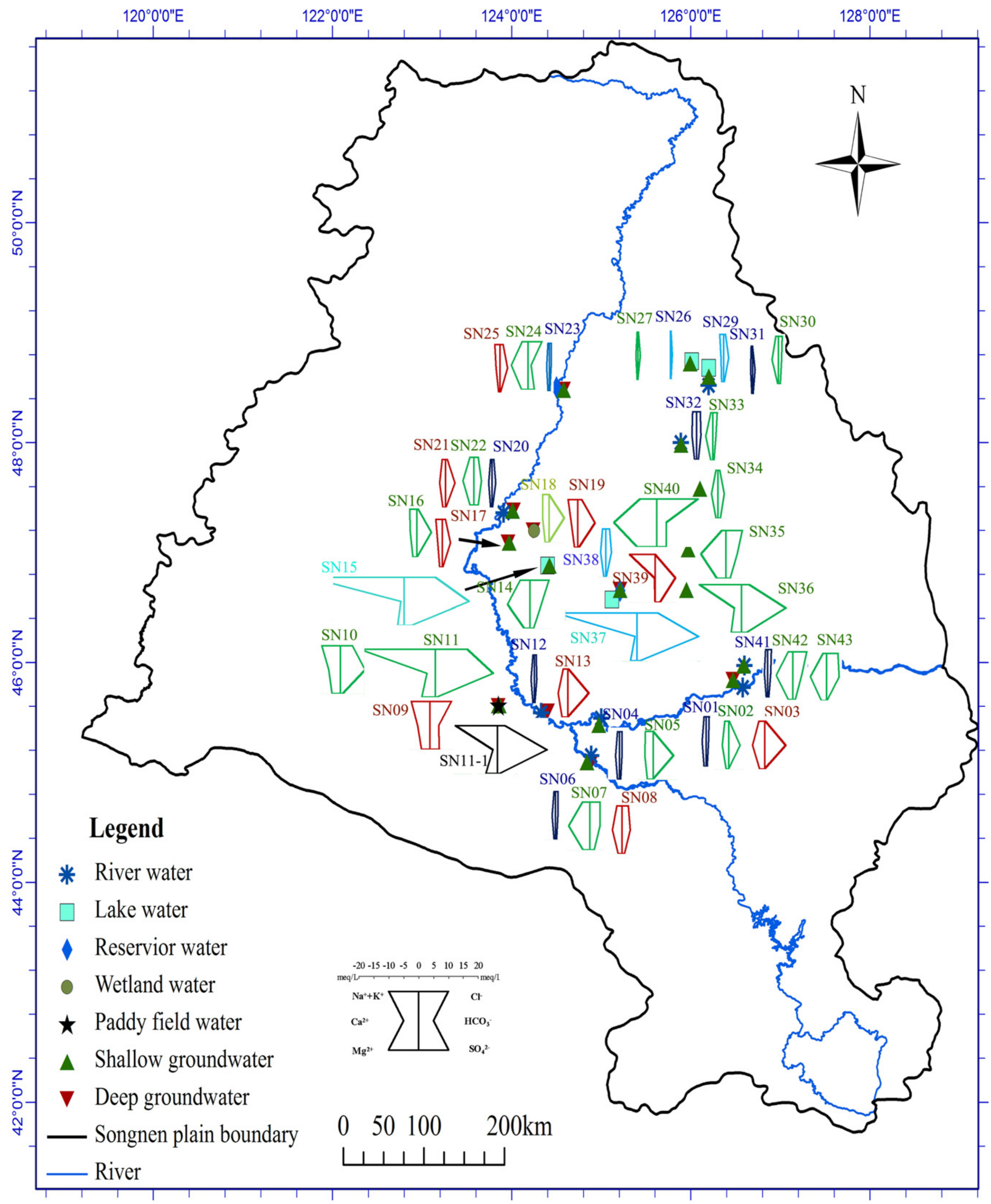

Fig. 3 – The hexa-diagrams of surface water and groundwater.

Table 2 – Water quality assessment by fuzzy membership.

Water samples		Number of samples within class					Total
		I	II	III	IV	V	
Surface water	River water	3	0	0	4	1	8
	Lake water	2	0	0	2	0	4
	Reservoir water	2	0	0	0	0	2
	Wetland water	1	0	0	0	0	1
	Paddy field water	1	0	0	0	0	1
Groundwater	Shallow groundwater	11	2	5	0	1	19
	Deep groundwater	8	1	0	0	0	9
Total		27	3	6	6	2	44

ion concentration of Na, HCO_3 and electrical conductivity significantly. The PC2 was correlated with ion concentration of Ca and NO_3. The third component was correlated with ion concentration of iron and water temperature. The PC4 was correlated with ion concentration of Mn negatively.

5. Discussion

5.1. *Drinking water quality*

The suitability for drinking water was evaluated by fuzzy membership according to the standards (Table 5). There are nine surface water samples that are suitable for drinking, contributing 56.25% of the total surface water samples (Table 2). The water samples within class IV and V contributed 37.5% and 6.25% of surface water, respectively. The concentration of iron in river waters exceeded the allowable values. Consequently the water samples were classified as IV and V. The lake water samples SN15 and SN26 were in class IV, exceeding in the concentration of iron. The concentration of iron in surface water is the key indicator which is greater than the guideline value.

The contributions of class I, II, III and V are 67.86%, 10.71%, 17.86% and 3.57% of groundwater, respectively. The shallow groundwater sample SN34 was in class II, and exceeded in the concentration of iron. The shallow groundwater in class III exceeded in the concentration of NO_3 and Fe. While the water sample SN22 in class V exceeded in the concentration of Mn. The concentration of SO_4 in deep groundwater sample SN39 in class II was larger than the allowable value. The exceeded water quality indicators of groundwater were mainly NO_3, Fe, Mn and SO_4. The contamination of nitrate indicates the human impacts on the hydrochemical composition in groundwater (Thyne et al., 2004). Thus, the high concentration of nitrate in shallow groundwater indicates that the water may be contaminated by agricultural activities.

The percentage of surface water and groundwater suitable for drinking was 81.82%, however, the class IV and V water samples contributed 18.18% (Table 2). The reservoir water and deep groundwater can be used as the drinking water resource. The river water and shallow groundwater had to be treated to remove and reduce the concentrations of Fe, Mn and NO_3 for drinking. The naturally occurring chemicals, Fe and Mn, in water exceeded the guideline values for drinking water. This result was caused by the unique geomorphology and the reduction environment in Songnen plain (Yuan, 2006). The most concentrated ions of Fe and Mn located in the center of the plain.

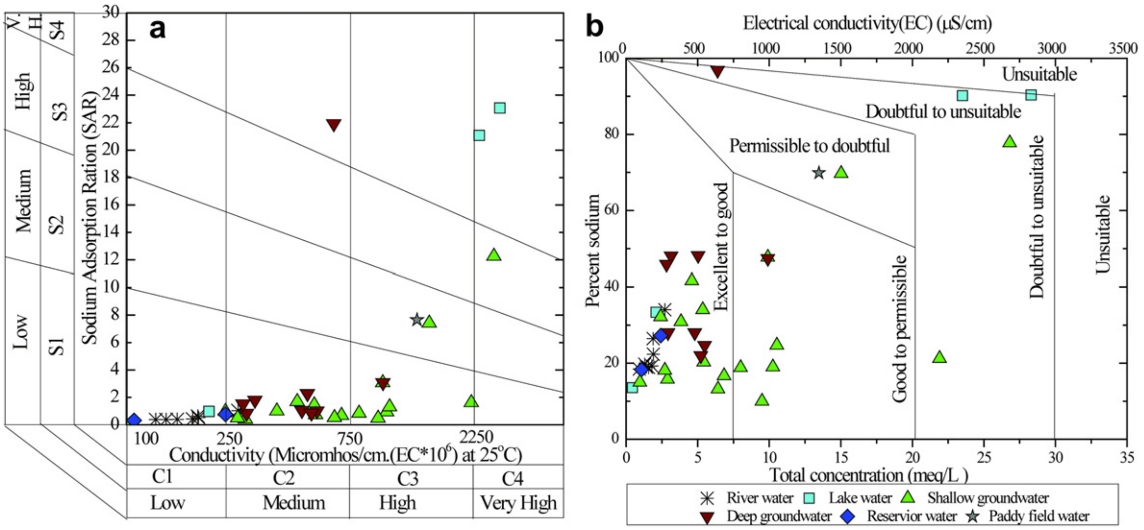

Fig. 4 – Diagram for irrigation waters classification (a) (after Richards, 1954), plot of percent sodium vs electrical conductivity (b) (after Wilcox, 1955).

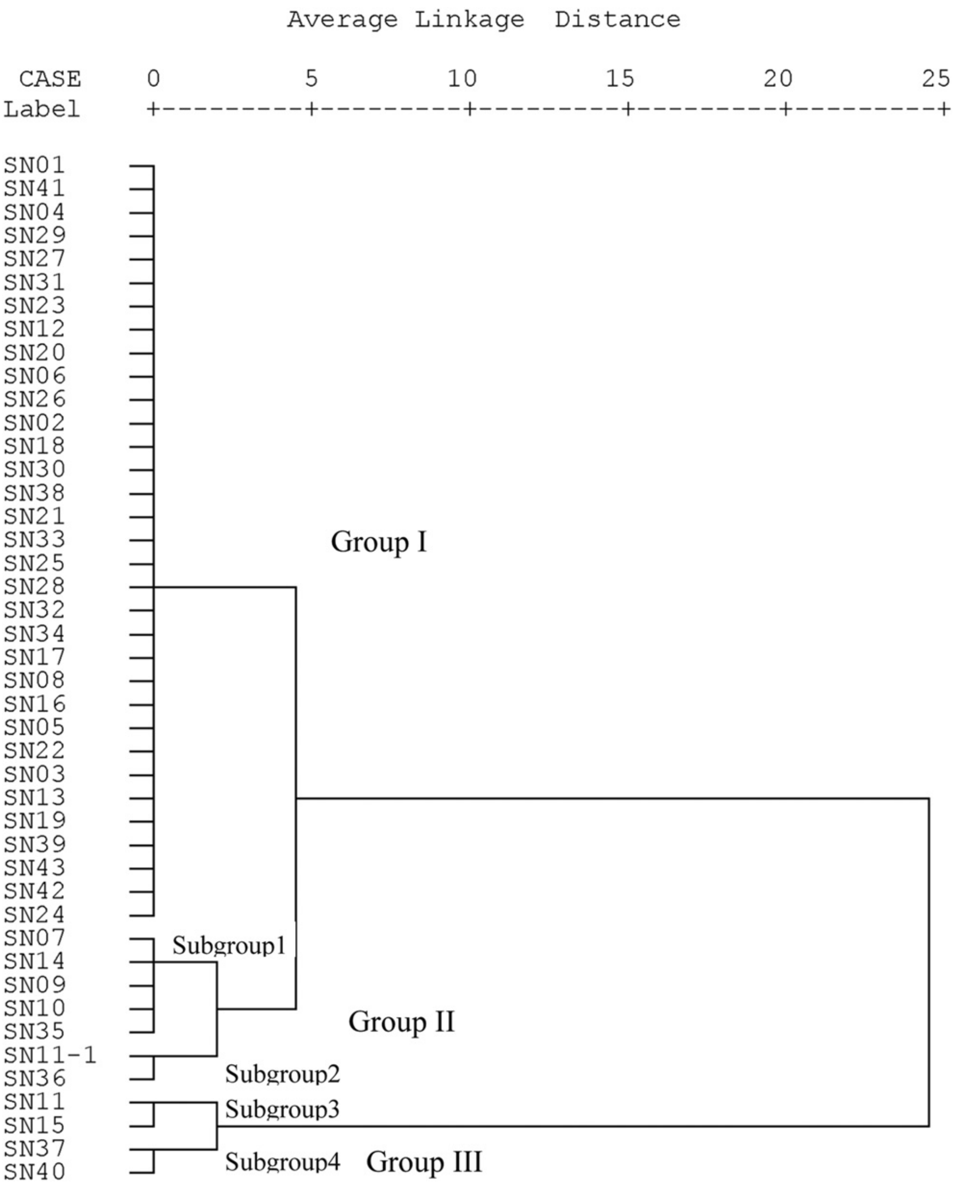

Fig. 5 – Dendrogram generated from HCA of water chemistry data.

5.2. *Irrigation water quality*

Songnen plain has been cultivated as one of the main grain production bases in northeast China. Groundwater provides about 40% of the water supply for irrigation, industrial and municipal use (Chen et al., 2010). The high quantity and quality of grain production depends on the water quality of irrigation water resource. Most of the surface water and groundwater were suitable for irrigation according to the water quality assessment by fuzzy membership. The percentage of class V that are not usable was only 4.54%.

The irrigation water quality evaluation by USDA classification diagram indicates that the percentage of excellent to good for irrigation was 70.45%. These water samples, falling in the category C1-S1 with low salinity and sodium can be used as irrigation water directly (Richards, 1954). The good to permissible irrigation water contributed 13.64% of water samples. The shallow and deep groundwater fall in category C2-S1 and C3-S1 with medium to high salinity and low sodium. These waters can be used as irrigation if amount of leaching and the drainage of soils occurs. The special management of salinity control and selecting of plants with good salt tolerance were required to reduce the salinity hazard risk. The percentages of permissible to doubtful and doubtful to unsuitable were 4.55% and 11.36%, respectively, with high to very high salinity hazard and medium to very high sodium hazard. The special sodium control and soil management were required to reduce the salinity and sodium hazard. Therefore, river and reservoir water were suitable for irrigation with little danger to the soil and crops. However, the sodium concentrated lake water, shallow and deep groundwater were required treatment before irrigation.

Table 3 – Mean water chemistry of the groups determined from HCA.

Group	Sub- group	n[a]	Ca	Mg	Na	K	HCO_3	SO_4	Cl	NO_3	Fe	Mn	EC	Tem	Class
I		33	1.68	0.72	1.16	0.09	2.33	0.37	0.91	0.10	0.27	0.16	338.07	14.43	II
II	1	5	5.17	2.17	3.19	0.05	3.77	1.42	4.59	1.25	0.04	0.03	1001.80	9.50	III
	2	2	1.62	3.13	11.59	0.27	13.27	1.09	2.14	0.18	0.00	0.00	1425.00	15.80	II
	Mean		3.40	2.65	7.39	0.16	8.52	1.26	3.36	0.71	0.02	0.01	1213.40	12.65	III
III	3	2	1.61	2.78	24.13	0.10	17.45	1.37	8.94	0.00	1.11	0.04	2755.00	14.35	IV
	4	2	6.33	3.73	13.87	0.07	10.08	1.76	8.85	3.33	0.23	0.00	2270.00	14.15	III
	Mean		3.97	3.25	19.00	0.08	13.76	1.57	8.89	1.66	0.67	0.02	2512.50	14.25	III

Units: pH (standard units), electrical conductivity (μs/cm), Tem. (°C), ion concentrations (meq/L), except Fe, Mn (mg/L).

a Number of samples within subgroups.

5.3. *Water quality indices*

To extract the efficient water quality indices, the fuzzy membership analysis and multivariate statistics method were applied. The water samples were gathered into five classes by fuzzy membership analysis. The surface water was classified into class I, IV and V, while the groundwater was classified into class I, II, III and V. Three groups were generated from HCA, and subgroups were classified into water quality level II, III and IV. The fuzzy memberships of subgroups classified by HCA were calculated by the mean values of hydrochemical variables. Therefore, the classification of subgroups was moderate without the class I and V. This shows that the fuzzy membership is an effective method to assess water quality according to standards. The HCA method is an objective and comprehensive way to group water samples by hydrochemical data (Güler et al., 2002).

Four principal components were extracted from PCA. The components were correlated with ion concentration of Na, HCO_3, Ca, NO_3, Fe and Mn significantly, as well as the EC and water temperature. There are large areas of soda saline-alkali soil distribute in Songnen plain. The ion of sodium is concentrated in water and soil. The variation of Na, Ca, HCO_3 were derived from natural weathering reaction, while the concentration of NO_3 is an indicator for anthropogenic impact (Thyne et al., 2004). The ion concentrations of Fe and Mn were correlated with the topography, reduction environment, aquifer media and water flow path (Zhang et al., 2007). The average ion concentration of nitrate in groundwater is 18 times of surface water (Table 1). This indicates that the groundwater is impacted of human activities, especially the usage of fertilizer and large quantity of irrigation. Consequently, the principal indicators to water quality assessment were Na, HCO_3, NO_3, Fe, Mn and EC. The ion concentrations of Na, HCO_3 are the indicators to sodium, and the Fe and Mn stand for the drinking water suitability. The electrical conductivity is a comprehensive index to ion concentration and quality assessment.

5.4. *Water quality management for sustainable development*

Water resource is the critical factor that influence the industrial and agricultural development. The precipitation decreased due to the Ease Asian monsoon and topography in Northeast China (Liang et al., 2011). This may cause the surface water and groundwater shortage with the increasing of population and grain production in this region. The

Table 4 – Principal component and varimax rotated component matrix.

Variables	Component matrix				Rotated component matrix[a]			
	PC 1	PC 2	PC 3	PC 4	PC 1	PC 2	PC 3	PC 4
Ca	0.634	−0.699	0.175	0.106	−0.064	0.904	−0.317	−0.103
Mg	0.896	−0.209	−0.093	0.104	0.504	0.736	−0.260	0.060
Na	0.723	0.640	−0.180	−0.128	0.970	0.096	0.171	0.047
K	−0.091	0.247	−0.199	0.530	0.042	−0.148	0.033	0.604
HCO_3	0.666	0.598	−0.370	−0.119	0.971	−0.002	0.000	0.094
SO_4	0.771	−0.143	0.266	−0.109	0.375	0.713	0.059	−0.213
Cl	0.934	−0.036	0.138	0.018	0.569	0.753	0.017	−0.041
NO_3	0.584	−0.560	0.369	0.308	−0.127	0.928	−0.062	0.071
Fe	−0.021	0.493	0.693	−0.145	0.063	−0.004	0.837	−0.202
Mn	−0.111	−0.167	0.157	−0.764	−0.069	−0.111	−0.020	−0.794
EC	0.947	0.271	−0.100	−0.060	0.861	0.491	0.003	0.008
pH	0.222	0.821	0.198	0.045	0.561	−0.156	0.631	0.165
Temp	−0.296	0.622	0.461	0.320	−0.066	−0.255	0.784	0.327
Eigen values	5.034	3.102	1.241	1.152	3.693	3.669	1.919	1.248
Variance (%)	38.72	23.86	9.54	8.87	28.41	28.22	14.76	9.60
Cumulative (%)	38.72	62.58	72.12	80.99	28.41	56.63	71.39	80.99

a Rotation method: varimax with Kaiser normalization.

Table 5 – Water quality standards for drinking and irrigation of surface water and groundwater.

Class[a]	Cl	SO_4	NO_3	Fe	Mn	TDS	Hardness	Suitability
I	50	50	8.86	0.1	0.05	300	150	Drinking, Irrigation
II	150	150	22.14	0.2	0.05	500	300	Drinking, Irrigation
III	250	250	88.57	0.3	0.1	1000	450	Drinking, Irrigation
IV	350	350	132.86	1.5	1	2000	550	Irrigation
V	>350	>350	>132.86	>1.5	>1	>2000	>550	Not suitable

Unit: ion concentration, TDS and hardness (as $CaCO_3$) (mg/L).
Data after (General administration of quality supervision inspection and quarantine of the people's republic of China, 1993, 2006; Ministry of environmental protection of the people's republic of China, 2002; Ministry of health of the people's republic of China, 2006).
[a] Allowable values of class I, II, III, IV.

relationship between surface water and groundwater not only impacts on the water quantity, but also on the water quality with the organic or inorganic compositions in water (Sophocleous, 2002). The rivers were discharged from groundwater in Northeast China (Zhang et al., 2011). Thus, the integrated water management, including water quantity and quality, surface water and groundwater, is the way to solve the water issue (Winter et al., 1998). The surface water and groundwater in the upstream are better than the water in the center of the plain. The sodium concentrations in surface water and groundwater in the central area are the largest. Consequently, the surface water in the upstream, including river water, reservoir water are suitable for drinking. However, the deep groundwater in the central plain could be used for drinking after the treatment of Fe, Mn and NO_3. Most surface waters are suitable for irrigation according to the standards. While, the surface water and shallow groundwater with high salinity, especially lake water, are required the salinity control to reduce the sodium hazard. Moreover, the new irrigation techniques are needed to enhance the agricultural irrigation efficiency (Pereira et al., 2002).

6. Conclusions

The surface water and groundwater were sampled and analyzed and assessed the water quality for drinking and irrigation. The fuzzy membership analysis is an effective method to assess water quality according to standards. Hierarchical cluster analysis is an useful method to group water samples. The indicators to water quality assessment were Na, HCO_3, NO_3, Fe, Mn and EC from principal component analysis. The high concentration of Na, Ca, HCO_3, Fe and Mn were correlated with natural environment conditions. The exceed concentration of NO_3 indicated anthropogenic impact on groundwater. The fuzzy membership and multivariate statistical techniques (HCA, PCA) are the useful and objective methods for water quality evaluations.

The reservoir water and deep groundwater can be used for drinking water. The river water and shallow groundwater can be used for drinking after removing and reducing the concentrations of Fe, Mn and NO_3 in water. Most surface water and groundwater were suitable for irrigation. River and reservoir water can be used for irrigation directly. But the concentrated lake water, shallow and deep groundwater were required treatment to reduce the salinity and sodium hazard. The integrated management of surface water and groundwater for drinking and irrigation is the way to solve water quality issues not only in Songnen plain, but also in other watershed.

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