ORIGINAL ARTICLE

Assessment of groundwater contamination by NO_3^- using geographical information system in the Zhangye Basin, Northwest China

Jing Fang · Yong-jian Ding

Abstract Geographical information system (GIS) technology was used to investigate NO_3^- concentration of groundwater in the Zhangye Basin, Northwest China. Thematic information and NO_3^- data of groundwater from the Zhangye Basin were analyzed in a GIS environment to study the extent and variation of NO_3^- concentration and to establish spatial relationships with corresponding land use types. About 38.8% of groundwater samples showed NO_3^- concentration above the human affected value (13 mg/l NO_3^-), while more than 10.2% exceeded the maximum acceptable level (50 mg/l NO_3^-) according to WHO regulations. The spatial distribution of NO_3^- of groundwater in the Zhangye Basin showed an obvious character of zonation; the high NO_3^- concentration was mainly located in the city seat areas, and Zhangye City was the high-value center. The probability of over 90% for NO_3^- concentration exceeding 13 mg/l was found in urban seat areas. The spatial analyses indicated that groundwater contamination by NO_3^- was closely related to one specific land use class, the urban. The NO_3^- concentration of groundwater under urban was significantly higher than that under irrigation land or sand dune. Most of the unacceptable NO_3^- levels were found in groundwater samples assigned to urban area, but a few were also found allotted to irrigation land class. Therefore, urban source was considered the principal source of NO_3^- contamination of groundwater in the Zhangye Basin, while irrigation land source was still a possible source of NO_3^- contamination.

Keywords GIS · NO_3^- concentrations · Land use · Zhangye Basin · Northwest China

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Introduction

Many regions around the world are entirely dependent on groundwater resources for the various uses, especially in arid areas. Groundwater can become contaminated naturally or because of numerous types of human activities. Residential, municipal, commercial, industrial, and agricultural activities can all affect groundwater quality (US EPA 1993).

Nitrate is the most frequently introduced pollutant into groundwater systems (Spalding and Exner 1993). Many studies show groundwater contamination by nitrate is a globally growing problem due to the population growth and increase of demand for food supplies. It usually originates from diffuse sources, such as intensive agriculture and unsewered sanitation in densely populated regions, or point sources such as irrigation of land by sewage effluent (Keeney 1986; Bouchard et al. 1992; McLay et al. 2001; Babikera et al. 2004; Sankararamakrishnan et al. 2008).

Elevated nitrate concentrations in drinking water can cause methemoglobinemia in infants and stomach cancer in adults (Lee 1992; Wolfe and Patz 2002). Groundwater with nitrate concentration exceeding the threshold of 3 mg/l NO_3^--N or 13 mg/l NO_3^- is considered contaminated due to human activities (the so-called human affected value;

Burkart and Kolpin 1993; Eckhardt and Stackelberg 1995). As such, the maximum acceptable concentration of nitrate for potable water according to the World Health Organization (WHO 1993) is 11.3 mg/l NO_3^--N or 50 mg/l NO_3^-.

Several approaches are developed to predict and estimate nitrate contamination from different sources. One approach applies solute leaching models (Addiscott and Wagenet 1985), which are difficult to calibrate and their boundary conditions cannot be easily satisfied in complex land use systems and nonuniform strata (McLay et al. 2001). Another approach correlates the dominant land use in an area and the actual nitrate concentration measured in the underlying aquifers (Barringer et al. 1990; Burkart and Kolpin 1993; Eckhardt and Stackelberg 1995; Ahn and Chon 1999; McLay et al. 2001). This approach is based on the assumption that land use influences the nitrogen flow in the surface soil and its consequent leach out into the groundwater. In all of these studies, agriculture is considered the most common land use related with nitrate contamination of groundwater.

The Zhangye Basin, located in the middle reaches of the Heihe River (Fig. 1), is an important agricultural and industrial center (Wang and Gao 2002). For the last few decades, surface water has been the main water supply for industries. However, as water demands have increased, groundwater is now used as a secondary water source. In the 1970s, the annual exploitation of groundwater was only 0.39×10^8 m³ and by 1999, this had hugely increased to 2.17×10^8 m³. Although recent studies reported that nitrate concentration in groundwater was high in areas of near urban and intensive agriculture (Zhang et al. 2004; Wen et al. 2008), but little direct evidence was provided to support the relationship between nitrate contamination of groundwater and land use.

Geographic information system (GIS) is a powerful tool and has great potential in aiding in the researches of environmental problems, as most environmental problems have an obvious spatial dimension. Spatially distributed models and GIS can interact, especially in the investigation of groundwater contamination and in the establishment of a spatial relationship between contaminated groundwater and pollution sources (Levallois et al. 1998; Ahn and Chon. 1999; Rodda et al. 1999; Babikera et al. 2004).

In this study, published thematic information and groundwater data from Zhangye Basin were used in a GIS environment to achieve two main goals. The first one is to characterize the extent and variation of nitrate contamination, and the second to investigate the spatial association between nitrate concentration and particular land uses.

Study area

Heihe River is one of the largest inland rivers in Northwest China, covering an area of 13×10^4 km². Its source is in the Qilian Mountains (Qinghai Province), it flows through the Zhangye Basin (Gansu Province), and the lower reaches (also known as Ejina Basin) are in the Inner Mongolia Autonomous Region (Fig. 1). The Zhangye Basin itself covers an area of 1.08×10^4 km² extending from 38°30′ to 39°50′N and 99°10′–100°52′E, and includes Zhangye City, Linze County and Gaotai County (Fig. 1). This area is characterized by an arid continental climate. Mean annual temperature is 3–7°C. Average annual precipitation ranges from 50 to 150 mm, with nearly 80% falling between June and September. Average annual potential evaporation is 2,000–2,200 mm (Gao 1991).

Fig. 1 Location map of study area and sampling sites 1
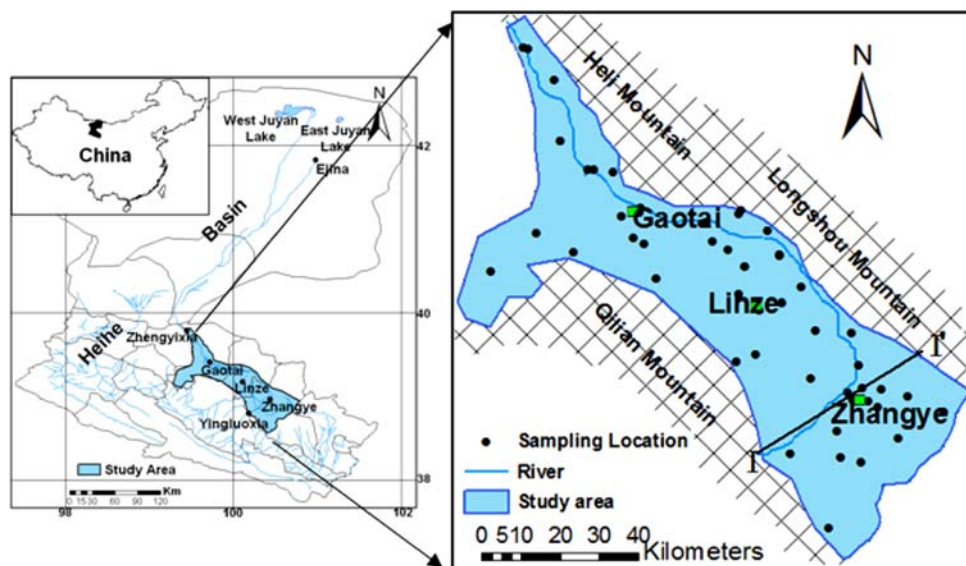
Hydrogeology

The hydrogeological setting of Zhangye Basin has been outlined by Fan (1981) and Chen (1997), varying from south to north. The southern part of the basin is an area of extensive faulting, underlain by bedrock. Down-faulted bedrock (pediments) extends toward the northeast, overlain by Quaternary sediments. The uplift of the Qilian Mountains caused the accumulation of several thousand meters of alluvial fan and fluvial deposits in a north–south trending basin, and filled with large volumes of unconsolidated Quaternary sediments, to depth of 300–500 m (Fig. 2). The Zhangye Basin can be divided into discrete geomorphologic units, including piedmont alluvial plain, alluvial plain, and desert. The sediments in the basin from south to north gradually change from coarse-grained gravel to medium and fine-grained sand and silt. These sediments, along with aeolian and lacustrine deposits, form the main aquifers. In the southern part of the Zhangye Basin, the aquifer is formed from highly permeable cobble and gravel deposits with a thickness of 300–500 m. From the northern edge of this diluvial fan, the aquifer becomes confined or semi-confined, with a thickness of 100–200 m, comprising interbedded cobble, gravel, fine sand and clay. Further north, the groundwater table becomes shallow (Fig. 2). A NW–SE thrust faults along the foot of the Qilian Mountains, it is difficult for groundwater to flow from the mountains into the basin laterally (Fan 1981; Chen 1997).The rivers originating from the Qilian Mountains are the main recharge sources for these aquifers. Under natural conditions, more than 70% of the surface water infiltrates into the aquifer. Groundwater in the basin generally flows from the piedmont area towards the center of the basin (Fig. 3). As the Longshou Mountains act as a barrier to groundwater flow, groundwater discharges at the middle and northern part of this sub-basin by upward seepage and springs. The depth to the water table ranges from 50–200 m in the upper alluvial fan of 3–5 m in the northern part of the floodplain.

Materials and methods

A total of 49 samples were collected for NO_3^- analysis during May and October, 2004. Samples were taken from the water-supplying wells and the long observation wells, with depth ranging from 8 to 240 m, and the location of sampling sites is shown in Fig. 1. The well locations were obtained by using a handheld global positioning system (GPS) receiver. Samples were collected in clean polyethylene bottles and dispatched for analysis to the laboratory in an ice-filled box. In the laboratory, samples were refrigerated at <4°C and the analysis was carried out within 48 h of collection. The concentration of NO_3^- was analyzed using a Dionex DX-600 ion chromatograph (precision is ±0.1%) at the Geochemistry Laboratory of the Cold and Arid Region Environmental and Engineering Institute, Chinese Academy of Sciences, Lanzhou, P. R. China.

A GIS software package Arcgis 9.0 was used to map, query, and analyze the data in this study. The land use map (1:100,000) was taken as a base map used to register and geo-reference other maps to guarantee optimum compatibility among various themes and hence, obtain reliable spatial relationships.

To investigate the spatial extent and variation of nitrate contamination, a nitrate concentration map was constructed from the point data using the ordinary kriging (OK) interpolation.

Fig. 2 Hydrogeological cross section along transect I–I' indicated in Fig. 1. *1* Gravel, *2* clay, *3* sand, *4* base rock, *5* fault line, *6* groundwater table, *7* borehole and depth
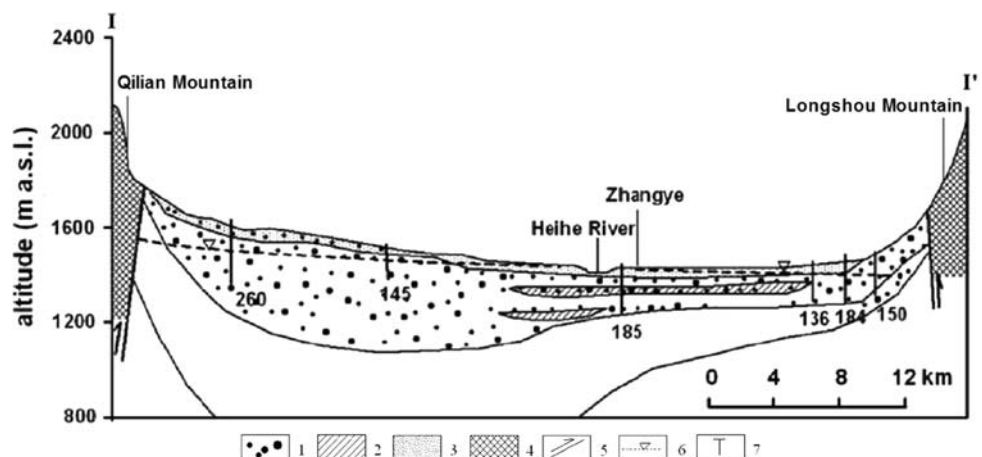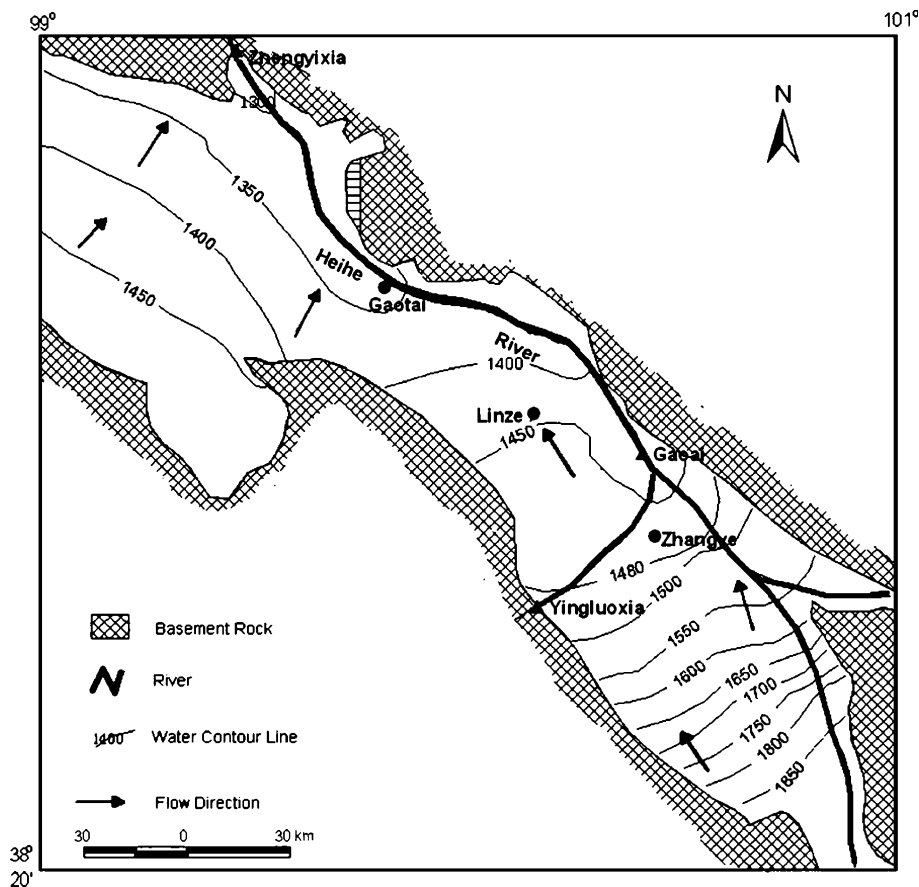
Fig. 3 Groundwater contours in the Zhangye Basin

Table 1 A statistical summary of measured NO_3^- (mg/l) constituents from groundwater samples

N	Max.	Min.	Average	SD
49	84.1	1.4	17.5	21.69

Results and discussion

According to the analysis of groundwater samples from the study area, the NO_3^- concentration showed a high degree of variability. The nitrate concentration ranged from 1.4 to 84.1 mg/l, with an average value of 17.5 mg/l (Table 1). The frequency distribution of NO_3^- concentration was presented in Fig. 4. The NO_3^- concentration was grouped into four classes: low (<13 mg/l), medium ($\geq$13 and <30 mg/l), high ($\geq$30 and <50 mg/l), and unacceptable ($\geq$50 mg/l), respectively.

The low class comprised samples with a low risk for human or the environment. The medium and high classes involved samples with NO_3^- concentration high enough to indicate the influence of human activities. NO_3^- concentration in the unacceptable class exceeded the recommendations for drinking water set by WHO (1993). Among the samples, less than 13 mg/l was found in 61.2%; thus, belong to the low class. The percentage of samples falling in the medium class was about 20.4% and the percentage of the samples falling in the high class was about 8.2%. About 10.2% of the samples exceeded the recommended maximum allowable value for nitrate in potable water according to the WHO (50 mg/l NO_3^-), which indicated that the groundwater had not been severely polluted by nitrate in this aquifer system. But the samples of groundwater exceeded the human affected value of 13 mg/l NO_3^- was near 38.8% (Fig. 4).

Variogram modeling

Geostatistics is used to characterize the spatial structure of the variable of interest by means of a consistent probabilistic model. This spatial structure is presented by the variogram, which describes how the variability between sampled concentrations increases with the increasing distances between the samples.

A transformation is a formula applied to all NO_3^- values in a data set in order to make its frequency distribution more normal. Lognormally distributed data, for example, can be made to follow a normal distribution more closely by applying the formula $\ln(NO_3^-)$ to each NO_3^- variate in the data set prior to the statistical analysis.
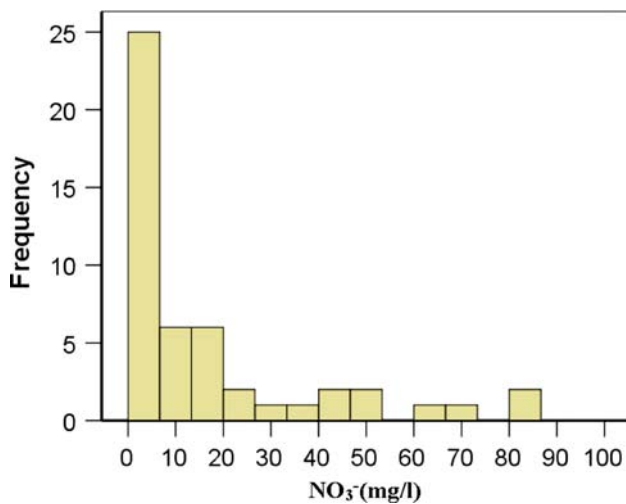
Fig. 4 Percent frequency distribution of NO_3^- concentrations

The experimental semi-variogram was calculated and the scatter plot of semi-variogram versus the distance classes was generated. By superimposing trials of various models (e.g. spherical, Gaussian and exponential) with different combinations of model parameters nugget, sill and range, the best approximation of the semi-variogram was selected. A Gaussian model was found to best fit the semi-variogram (Fig. 5). The spatial correlation distance of NO_3^- concentration was 7,800 m (Fig. 5).

Spatial distribution of NO_3^-

The contour maps, generated by the selected semi-variogram model and ordinary kriging method, indicated that the spatial distribution of NO_3^- of groundwater in the Zhangye Basin was of zonation (Fig. 6). In detail, the high NO_3^- concentration was mainly located in the city seat
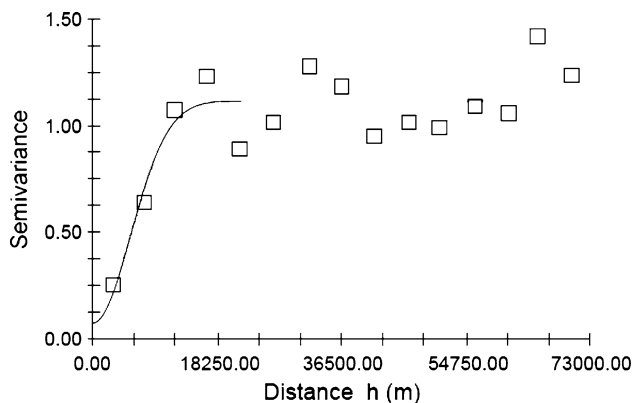

Fig. 5 Semivariogram of NO_3^-. Gaussian model (nugget = 0.082; sill = 1.119; range = 7,800.00; $r^2 = 0.746$; RSS = 0.278)
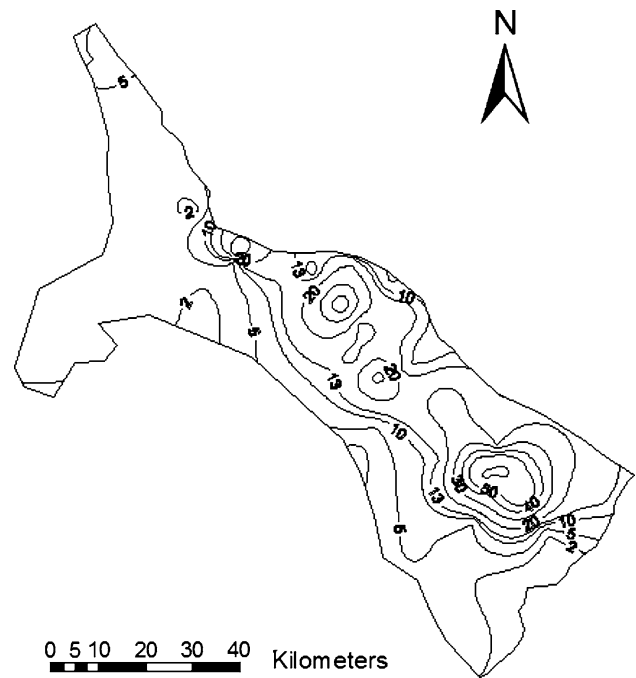

Fig. 6 Spatial distribution of NO_3^- of groundwater in the Zhangye Basin

areas (Fig. 6). Zhangye City was the high-value center where the maximum NO_3^- value was 84.1 mg/l, and Linze City and Gaotai City were the other high-value centers of NO_3^-. In the city seat areas, a considerable quantity of domestic sewage and industrial wastewater with high levels of NO_3^- were drained into the surrounding lands, which resulted in high NO_3^- concentration in groundwater (Zhang et al. 2004). In the front of the Mountain plain, the concentration of the NO_3^- was less than 13 mg/l. And because the front of the Mountain plain was the main recharge source for the aquifers, the most likely background concentration of NO_3^- in groundwater could be regarded as 13 mg/l. In the northern part of the basin, the concentration of NO_3^- in groundwater varied from 2 to 5 mg/l, which was less than the 13 mg/l, and this pattern was considered a result of the disappearance of nitrate by natural denitrification.

To get a better appreciation of the spatial distribution of NO_3^- concentrations across the Zhangye Basin, the conditional probability of the NO_3^- concentration exceeding the value of 13 mg/l (the human activities affected value) is shown in Fig. 7. The probability over 90% for NO_3^- concentration exceeding 13 mg/l was found in four distinctive regions: Zhangye City, Linze City, Gaotai City and the northwestern Linze area, respectively. The city seat areas associated with intensive human activities had certainly high nitrate concentration of groundwater exceeding the human affected value of 13 mg/l. In the front of the Mountain plain and the north part of the basin, the
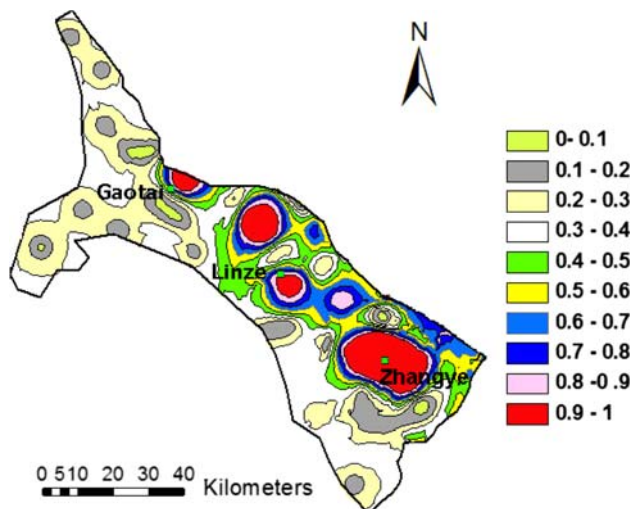
Fig. 7 Probability map of NO_3^- concentration exceeding the value (13 mg/l)

probability of the NO_3^- concentration exceeding the value of 13 mg/l varied from 0 to 40%.

Groundwater NO_3^- contamination and land use

Further analyses were conducted to assess NO_3^- concentration of the Zhangye Basin for the different land use classes. Many studies in literature had investigated the relationship between land use classes and nitrate concentration in groundwater, but few were carried out for the Zhangye Basin. The main statistics of nitrate concentration for the different land use classes is summarized in this study (Table 2).

Comparison of NO_3^- concentration among the different land use classes indicated that the boreholes located under the ''Urban'' class had characteristically high average NO_3^- concentration (41.81 mg/l), followed by those located under the ''Irrigation land'' class (14.77 mg/l) and the ''Sand dune'' class (13.42 mg/l) (Table 2).

The spatial relationships between the different land use units and NO_3^- concentration levels of groundwater are displayed clearly (Fig. 8). The relationship between NO_3^-
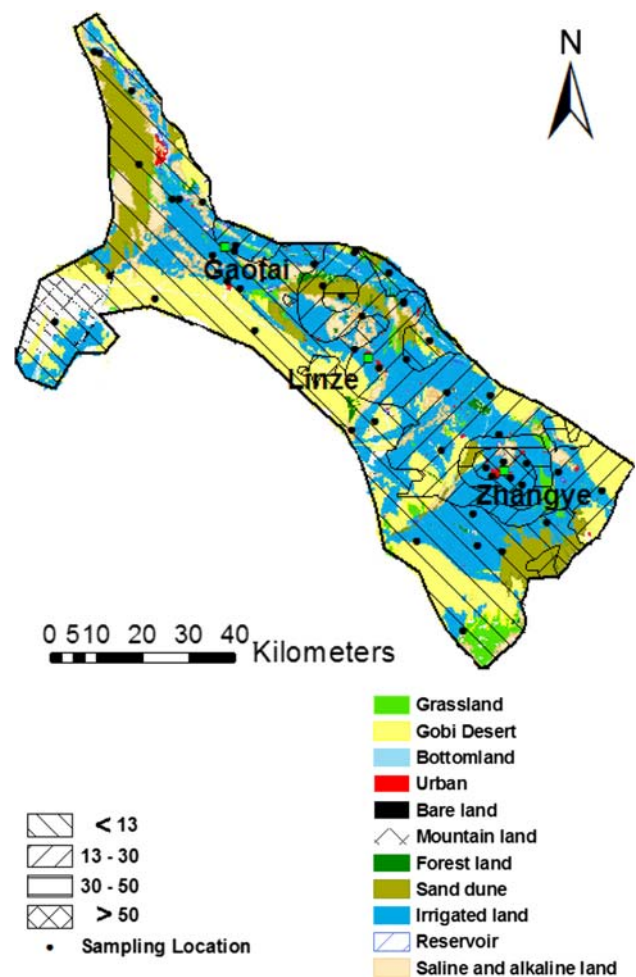
Table 2 Statistical comparison of nitrate concentrations [NO_3^- (mg/l)] among different land use classes

Land use class	N	Max.	Min.	Average	SD
Irrigation land	27	68.60	1.40	14.77	18.90
Urban	9	84.10	5.00	41.81	31.52
Sand dune	3	27.44	3.96	13.42	11.44
Gobi Desert	5	4.66	2.53	3.39	0.83
Saline and alkaline land	5	11.00	2.15	7.13	3.93

Fig. 8 The spatial association between land use and nitrate (NO_3^-) contamination defined by level of NO_3^- concentration

contamination and urban in the Zhangye Basin was obvious. Zhangye City had the high content of NO_3^- involved in unacceptable NO_3^- concentration (>50 mg/l). Linze City and Gaotai City were associated with medium (≥ 13 and <30 mg/l) NO_3^- concentration. About 67% of irrigation land area was associated with medium (≥ 13 and <30 mg/l) NO_3^- concentration, which could be attributed to fertilizer use in vegetative production. In the northwest of Linze City, the overlap area of the ''Sand dune'' class was associated with high (≥ 30 and <50 mg/l) NO_3^- levels in the groundwater, which could be caused by the nitrate-rich water spreading out from the surrounding highly contaminated zone and extra evaporation. The Gobi Desert, sand dune and irrigation land located in the front of the Mountain plain and the north part of the basin class were associated with low (<13 mg/l) NO_3^- levels in the groundwater.

Therefore, urban source was considered the principal source of nitrate contamination of groundwater in the

Zhangye Basin, while it was still possible that nitrate contamination came from irrigation land source.

Groundwater level is dropping continually because of the intensive development of groundwater in research region. Wide exploitation results in not only the incrassation of vadose zone, but also the change of nature circle way of groundwater. Thick vadose zone can also form following the formation of the cone of depression. And because vadose zone is involved in the infiltration of contaminated solution, the drop in water level and the hugely thick vadose zone aids in the chemical conversion and biolysis of pollutant.

Point sources and diffuse sources are the main sources of groundwater NO_3^- contamination. The former include urban sewage, industrial wastewater, domestic discharge and wastewater from metal mine. The latter include the irrigation of land by sewage effluent, intensive application of nitrogen fertilizer and organic fertilizer. Besides the dissolution of nitrate mine, the high content of NO_3^- in groundwater can be caused by domestic discharge, industrial wastewater and the runoff and infiltration from the fertilized land. In this study, comparing the outcome of data analysis with the sampling surrounding conditions, it was concluded that different values of NO_3^- concentration in different regions reflected the impact of human activities and environmental conditions on the groundwater, and that high nitrate in groundwater were found in urban city.

Point sources are important factors affecting the nitrate content in groundwater. In the study area, littering municipal solid water (MSW), dejecta and livestock discharge, infiltration of plenty of untreated sewage via seepage wells or seepage pits and the leakage of sewage tanks all result in the increase of NO_3^- concentration. In Zhangye City, annual average domestic discharge is as high as 5.1×10^6 m^3, and annual drainage of wastewater from industrial production and the other sources amounts to 2.6×10^6 m^3. The domestic sewage mainly comes from the household and the tertiary industry, which is discharged to suburbia for irrigation and greening after being disposed untreated. Therefore, in this region, the discharge of industrial wastewater and domestic sewage are the key factor that results in the NO_3^- contamination in groundwater.

Diffuse sources are the other important factors. The majority of the research region is occupied as irrigation land because the agriculture is the local leading industry. Nitrogen fertilizer application may be the important source of the NO_3^- contamination in groundwater. The N use efficiency in research region is only 30–50%, lower than the value of 60–70% in the advanced countries reported by Food and Agriculture Organization (FAO). Accordingly,

the application of fertilizer may the other important factor results in the nitrate contamination.

Only preliminary conclusion can be drawn about the pollution sources of NO_3^- contamination in groundwater based on the analysis above. To obtain more precise and fuller conclusion on the sources of NO_3^- contamination, the further study should be carried out on the values of N isotope of nitrate in groundwater.

Summary and conclusions

This study employed the geographical information system (GIS) technology to investigate NO_3^- concentration of groundwater in the Zhangye Basin, Northwest China. Thematic information and chemical data of groundwater from the Zhangye Basin were analyzed in a GIS environment to study the extent and variation of nitrate contamination and to establish spatial relationships with corresponding land use types.

The recommended maximum allowable value for nitrate in drinking water according to the WHO of 50 mg/l nitrate exceeded in 10.2% of the samples collected, indicating that the groundwater had not been severely polluted by nitrate in this aquifer system. About 38.8% of the samples of groundwater exceeded the human affected value of 13 mg/l NO_3^-.

The spatial distribution of NO_3^- of groundwater in the Zhangye Basin showed an obvious feature of zonation. The high NO_3^- concentration was mainly located in the city seat areas, and Zhangye City was the high-value center where the maximum NO_3^- value (84.1 mg/l) was determined. The probability of over 90% for NO_3^- concentration exceeding 13 mg/l was found in four distinctive regions. These regions correspond to Zhangye, Linze, Gaotai City and the northwestern Linze area.

The spatial data analyses with GIS displayed the close relationship between NO_3^- contamination of groundwater and one specific land use class, the urban. Groundwater samples under the urban class showed the highest average nitrate concentration, followed by those under irrigation land class and sand dune class. About 67% of irrigation land area was associated with medium (≥ 13 and <30 mg/l) NO_3^- concentration. Therefore, urban source was considered the principal source of nitrate contamination of groundwater in the Zhangye Basin, while irrigation land source was still the possible source of nitrate contamination.

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