Comparative health risk assessment of nitrate in drinking groundwater resources of urban and rural region(Isfahan, Iran), Using GIS

Saba Aghapour
Isfahan University of Medical Sciences
Bijan Bina
Isfahan University of Medical Sciences
Mohammad Javad Tarrahi
Isfahan University of Medical Sciences
Fahimeh Amiri
Water and Wastewater Equipment Manufacturers Association
Afshin Ebrahimi (a_ebrahimi@hlth.mui.ac.ir)
Isfahan University of Medical Sciences https://orcid.org/0000-0002-3640-087X

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Abstract

Background : Groundwater contaminant such as nitrate (NO 3 -) is one of the environmental factors that can affect human health . Methemoglobinemia of infants, thyroid disorders, and probably some carcinogenic effects, are health concerns associated with dietary nitrate. Isfahan province has a dry and semi-arid desert climate that the main source of various applications in this province is groundwater resources. This study evaluated spatial analysis of the concentration of NO 3 - in groundwater resources and its possible health risk to residents. Results : It was indicated that nitrate concentrations in the rural and urban areas were in the range of 0.4–137 mg/L NO 3 – with the mean of 33.72 mg/L NO 3 – , and 2.9-209 mg/L NO 3 - with the mean of 38.87 mg/L, respectively. As well, 226 samples (25%), and 104 (24%) ones were detected above the Iran and World Health Organization guidelines 50 mg/L as NO 3 – . While the highest levels of NO 3 – which were located in the west and central groundwater resources of the province were in the agricultural and residential areas. The HQ for Infants, in 32% of samples, urban 136 and rural 297 samples were higher than 1 (HQ>1). Also, in urban area HQ was more than 1 in 8, 5, 1, and 3 samples in children, teens, male and female, respectively. Conclusions : Infants were the most vulnerable compared with the other groups. Therefore, in some areas, there are potential risks of methemoglobinemia, especially for infants. So, it is critical to adopt specific strategies to reduce the nitrate concentration in the studied groundwater.

Background

Groundwater is vulnerable to contamination by nitrate (Wongsanit et al., 2015). High nitrate level in groundwater has been reported worldwide the late after decades (Ghiglieri et al. 2009;Cheong et al. 2012; Pennino et al. 2020). Agricultural activities (inorganic fertilizers, organic nitrate livestock manures), wastewater, industrial wastes, animal breeding operations, landfill leachate, soil organic nitrogen and atmospheric deposition of nitrogen oxide compounds are probably the most important local source to increase the nitrate contamination of groundwater (Gao et al., 2012; Lassaletta et al., 2009; Zirkle et al., 2016). $NO_3^-$is a highly soluble compound that is not bound to the soil, so, it readily leaches into groundwater or surface water (IARC, 2010). Nitrate levels in groundwater are influenced by several factors, such as climate, groundwater age, soil type, nitrogen sources geochemistry, the land surface area contributing to the wells and travel time in the aquifer (Matiatos, 2016). Risk assessment models and spatial analysis can be used to identify potential nitrate sources and to evaluate the factors controlling the nitrate concentration in groundwater (Bian et al., 2016; Hu et al., 2005; Jamaludin et al., 2013; Rojas Fabro et al., 2015; Saidi et al., 2011; Shrestha et al., 2016). In a nitrate risk assessment of groundwater research in South Korea, the nitrate level was evaluated 79.4 mg/L, as a result of the risk analysis in the agricultural area. In other words, some of the studied groundwaters exceeded the Korean drinking water standard (Cheong et al., 2012). Groundwater nitrate risk assessment in Northern Ireland was conducted for diffuse agricultural sources, by using an improved GIS-based D-DRASTIC approach. The results showed that very high and high zones of groundwater nitrate risk occupy 5% and 11% of the case study area, respectively (Wang and Yang, 2008). (Bian et al., 2016) in China showed the high-risk area accounted for 88.78% of the total study area. The results of probability risk model with simulations and geostatistics for mapping of the health risk in Spain showed that waterborne health risk coefficient by nitrate-polluted water for 10% of the surface of the study area was more than 1, where the municipalities with the highest contamination thresholds are located at agricultural activity area (Chica-Olmo et al. 2017).

Excessive concentration and chronic nitrate exposure can be toxic for both humans and animals (Enwright and Hudak, 2009). Scientific studies showed that exposure to nitrate in drinking water containing concentrations above 45 mg/L has been implicated as a causative agent in infants methemoglobinemia. Generally, after three months, an enzyme is produced in the human body that restores the ability of hemoglobin to carry oxygen, for this reason, infants under three months of age are known to be a vulnerable population (IARC, 2010; WHO). Recent studies have also shown a weak association between exposure to nitrate levels above 50 mg/L in drinking water and changes in thyroid gland function and birth defects. In this regard, infants and pregnant women are known as the sensitive populations (Bahadoran et al., 2015; Gilchrist et al., 2010). Many of N-nitroso compounds (NOCs) are carcinogenic which can be produced with long-term exposure to nitrate and nitrite. In the human body, nitrate reduce to nitrite, while these compounds are not themselves carcinogenic, this health concern is that nitrate could be metabolized to N-nitroso compounds, and increase the probabilities of cancer occurrence for adults (Bedale et al., 2016; Gilchrist et al., 2010; Klein et al., 2013). Although these effects are low in some isolated studies and epidemiological studies have not demonstrated consistent relationships between nitrate exposure and the risk of any type of cancer (Eichholzer and Gutzwiller, 1998). However, it is possible that exposure of nitrate in drinking water above 45 mg/L estimate the cancer risk related to a known nitrosamine, Nitrosodiethylamine (NDEA) (Bahadoran et al., 2015; Barnes et al., 1988; Gilchrist et al., 2010). International agency for research on cancer (IARC 2010) has established a nitrate classification in group 2A, which is probably carcinogenic to humans. United States Environmental Protection Agency has established a maximum contaminant level of 45 mg/L for nitrate ion, based on methemoglobinemia in infants. WHO guideline values and national standard of Iran is 50 mg/L of NO_3^- in drinking water for infant methemoglobinemia (WHO, 2011). The major pathways of human exposure to nitrate are food and drinking water, more than 80% of dietary intake of nitrate is attributed to vegetables (Bahadoran et al., 2016). Individual's nitrate intake of food and water depending on vegetable consumption and the local concentration of nitrate in drinking water, in the U.S. dietary nitrate intake is generally about 40–100 mg per day. The World Health Organization has established acceptable daily intakes (ADI) levels of nitrate (3.7 mg nitrate/kg.day), based largely on drinking water standards. Water is a major source of nitrate intake at concentrations above 50 mg/L (EPA, 2015). Groundwater resources are an important source of drinking water in the world, so, most of them are used without treatment. Thus, to preserve the quality of them is critical (Ashrafzadeh et al., 2016; Zheng and Ayotte, 2015).

Isfahan province is located central plateau of Iran, and has a semi-arid and dry desert climate, groundwater resources are important and the main source of drinking water sources in the region, especially for the rural areas. Also, in this area, there are more agricultural and industrial activities. It is advisable to incorporate studies on health risk and nitrate concentration in the management of groundwater resources. The data available for the quality control of water resources shows an increase in nitrate concentration in Isfahan. This study aims to investigate the distributions of nitrate level in drinking groundwater resources and its effect on human health in Isfahan province using Geographic Information System (GIS) for the identification of risk areas. The results of this study would be useful for all stakeholders, international, national, and regional decision-making organizations in safe drinking water supply for both excessive and insufficient nitrate content and Isfahan to prevent long-term potential health risks. Besides, this information may be useful for future water resource planning for this area.

Materials And Methods

Study area

The study area, Isfahan province (49°38’ to 55°32’ E, 30°42’ to 34°27’ N), is located in central Iran (Fig. 1). It covers an area of about 107,027 km^2. The topography consists mainly of a flat plain, forest, with the River Zayandehroud which flows from the west to southeast in central Iran. It is divided into 24 counties and 34 aquifers. The residential population was around 4,686,930 people. The geology of Isfahan is dominated by primary granites, especially in alkali-rich granites, red-colored conglomerate without fossil, yellow marl, or gray-limy grayish, grained or red sandstone and gray schist, stones of calcareous dolomite, and lime. The height of the province's various regions varies from less than 500 meters in the east to more than 4000 meters in the west and with the main average of 1660 meters. This region is a very productive agricultural area, industrial sites, urban, and uncultivated lands (Fig. 2). Thus, groundwater quality will be affected by diffuse contamination originating from these activities. Most rainfall occurs in the western regions. The average annual rainfall is about 150 millimeters. Isfahan province has a semi-arid and dry desert climate with hot summer and maximum temperature around 36°C and cool winter with an average temperature of 5.7°C (68.9, 26, 5.1 percent of the area of the province has dry, semi-dry, and wet climate, respectively). It has a warm and semi-dry climate in the north and east parts and cold climate in the south. The main urban water supply (Isfahan city and around) comes from surface water, Zayandehroud river. Whereas, in the rural areas and counties, the drinking water source is provided from the groundwater resource.

Sample collection and analysis

This study was implemented with the cooperation of Isfahan Water & Wastewater Company for the sampling of the drinking groundwater resource. This company has the most exhaustive sampling program in the study area and controls quality and quantity drinking water networks in the region. We obtained 1319 nitrate measurements from all resources and counties in Isfahan province, from March 2018 to February 2019. Groundwater samples were taken from 1178 tube wells, 90 springs, and 51 Qanats as the drinking water sources in the region. The 30.4%, 32.1%, 12.1%, and 25.4% of water samples were analyzed were related to spring, summer, fall, and winter, respectively. The 891 samples were taken from groundwater resources located in rural areas and 428 samples in urban areas. Samples were collected after a period of pumping. Also, the temperature and geographical positions of the samples were recorded using a portable GPS during the sampling. The samples were taken under standard conditions and transferred to the laboratory in plastic containers and then were analyzed within 24 h. The concentration of nitrate was measured by the SPADNS method using a DR-5000 Hach-Lange spectrophotometer, USA (355 programs, 500 nanometers). Electrical conductivity (EC) and pH were measured by a portable EC meter (wtw) at the field, and chloride ion was measured by following the standard method (APHA 2005).

Exposure and Health risk assessment

Health risk assessment evaluates the probability of adverse health effects on human health upon exposure to contaminants for a certain period. It provides a systematic approach for developing a management strategy to supply safe drinking water. Hazard quotient (HQ), the US-EPA probabilistic model was used for Non-carcinogenic risk assessments, which is defined as the ratio of the estimated dose of a contaminant of the reference dose (RfD) (EPA 1989). The method can show the population's non-carcinogenic health risk levels as a consequence of nitrate intake. The population was divided into the following four age groups because of physiological and behavioral differences: infants (3 months' age); children (0–10 years old); teens (11–20 years old); and adult males, and females (21–72 years old).

Non-carcinogenic health risk of nitrate from drinking water intake was calculated for various populations as follows (EPA 1989):

$$EDI = \frac{C \times IR}{BW}$$

1

$$HQ = \frac{EDI}{RfD}$$

2

where EDI is the estimated daily nitrate intake dose through oral exposure pathway per unit weight (mg/kg/day), IR is the drinking water ingestion rate (L/day), C is the nitrate concentration in drinking water (mg/L), and BW is body weight (kg), HQ that represents the methemoglobinemia risk from drinking water is considered to be the hazard quotient, of which a value lower than 1 implies a negligible risk of non-carcinogenic effects, whereas HQ greater than 1 indicates potential non-cancer causing health effects. RfD is the threshold dose below which no carcinogenic toxicological effects exist on the individual exposed for the exposure time considered. An RfD value of nitrates equal to 1.6 mg//kg/day has been estimated based on) EPA 2015).

In the study area, calculations for non-carcinogenic health risks associated with the consumption of groundwater containing nitrate by the residents were made using the standard assumptions used in US-EPA risk analysis. The exposure parameters and their probability distributions for the four age groups are presented in Table 1.

Table 1. Reference dose (RfD), body weight (BW) and Ingestion rate (IR water) used in the present study

Distribution type	Parameters	Value	Unit	Reference
Infants	Ingestion rate	0.64	L/day	
Children	(IR water)	1		
Teens		1.7		
Male		2.4		
Female		2.3		
Infants	Body weight (BW)	4	Kg	(EPA, 2011)
Children		20		
Teens		54		
Male		75		
Female		69		
Oral reference dose	RfD	1.6	Mg/kg.Day	(EPA)

Mapping and Statistical Analysis

Study area map with sampling point locations, nitrate distribution, and other parameters were created by using ArcGIS10.2. GIS allows spatial data gathering, at the same time, gives a means for data processing such as geo-referencing, digitizing, and spatial analysis. The Inverse Distance Weighting (IDW) method was chosen for interpolation and the best prediction approach for concentrations zoning maps of nitrate in the study area. For the other maps, the classification by size and color symbol was used. The SPSS 20 software was used for data analysis. Correlation calculations and basic statistics were carried out.

Results And Discussion

The NO_3^- concentration was monitored in 1319 water samples taken from all drinking groundwater resources in Isfahan province.

Nitrate concentration in groundwater

Nitrate in the rural area had a range between 0.4–137 mg/L NO_3^- with the mean of 33.72 mg/L NO_3^-, also in urban area, it was 2.9–209 mg/L NO_3^- with the mean of 38.87 mg/L NO_3^-. One-sample T-test showed that there was a significant difference between the NO_3^- concentration in the samples concerning the (WHO) guidelines and also the Iranian national standard (50 mg/L) ($p < 0.001$). The mean NO_3^- concentration of samples was lower than the standard level but, 25% of the samples, 226 rural and 104 urban samples had nitrate levels > 50 mg/L NO_3^-, above the acceptable level. Most of the sources are well in the study area and 89% of samples were of these sources. Qanats sources have located in the central area and springs sources in the south and east of the province. The highest nitrate concentrations were in well water sources, while the lowest was in spring ones ($p < 0.001$). It is noted that in spring sources possible pollution is low because there are located in highlands and low anthropogenic activities areas. While near pollutant points sources and different depths of wells could be probably the main cause of the high concentration of nitrate in wells.

The NO_3^- levels in rural and urban areas with seasonal variations are shown in Table 2. One-way analysis of variance (ANOVA) showed that there was a seasonal significant difference in groundwater NO_3^- concentrations ($P < 0.002$). The fall season had the highest concentration with mean concentration 46.51, 47.98 mg/l in rural and urban, respectively, while, spring season with 32.59, and 30.15 mg/l had low concentrations. Figure 2 shows precipitation values in months of 2018 in Isfahan province. These high concentrations might be due to precipitation in fall and winter, which dissolve the NO_3^- contents of soils in groundwater resources. (Shrestha et al., 2016) indicated that the concentration of chemicals in the water resource may be influenced by weather conditions. Many studies showed nitrate levels in groundwater increase during the wet weather season and decrease during dry and warm weather. But some studies showed the opposite results. In a study (Jamaludin et al. 2013) in Malaysia, the reason for low concentration in regaining was sampling in the rainy season and after fertilizing lands. (Baghapour et al., 2014) showed no difference in dry and wet seasons of Shiraz city water resources, south of Iran, because the plain texture is impervious. (Gao et al. 2012) reported NO_3^- concentration in July and September was high and difference season is in NO_3^- concentration in an agricultural and residential area in china. Also, in Isfahan province cultivates various crops with consumption of different water and different cropping system by fertilizer value might because to change level and direction groundwater.

Table 2

The NO_3^- concentration of the samples in rural and urban areas with seasonal variations

		NO_3^-(mg/L)			
		Rural	N.S	Urban	N.S
Spring	Mean	32.59	287	30.15	113
	Std. Deviation	24.96		18.34	
	Minimum	0.9		3.21	
	Maximum	132.9		85.1	
Summer	Mean	33	285	37.2	139
	Std. Deviation	22.34		30.14	
	Minimum	0.4		4.58	
	Maximum	123.88		183.15	
Fall	Mean	**46.51**	89	**47.98**	71
	Std. Deviation	25.68		42.46	
	Minimum	3.5		2.9	
	Maximum	115.4		209.14	
Winter	Mean	33.45	230	40.15	105
	Std. Deviation	23.27		34.29	
	Minimum	2.9		5.96	
	Maximum	136.9		195.5	
N.S: Number samples					

Malekabadi et al. showed high concentration in last winter and the beginning of spring due to dissolve nitrate leaching caused by the winter precipitations and start the planting season (Malekabadi et al. 2004). Also, agricultural activities and river pollution due to wastewater, drainage agricultural were the important causes of groundwater pollution in the Zayandehroud river basin.

The maximum NO_3^- concentrations in the groundwater resource of each county are shown in Fig. 3. The results show that there is consistency in concentrations in rural and urban groundwater resources. The samples of the highest NO_3^- level were detected in Ardestan, Buyin and Miandasht, Dehagan, Falavarjan, Frydan, Fraydonshahr, Kashan, Khansar, Lenjan, Mobarakeh, Natanz, Najafabad, Nayin, Shahinshahr, and Tiran. This may be due to the geological structure because of gypsum and salt tissue present in their soils, or depth of the well can be the reason for increasing NO_3^- in groundwater in these regions. Najafabad city had the highest concentration because of the agricultural area. These findings are inconsistent with the results obtained by (Malekabadi et al. 2004) in groundwater of Najafabad, Natanz, Shahrreza, Isfahan, and Kashan cities that showed high NO_3^- concentration was in March and April. In the study of the nitrogen pollution and the transformation processes of NO_3^- in the urban area of Del Campillo city and its surrounding rural area with different land-use types, showed the urban area had the more nitrate concentrations than the rural area. Furthemore, denitrification processe in groundwater in the urban area was higher than the rural area (Blarasin et al. 2020).

Spatial distribution of Nitrate

GIS techniques were suggested for the vulnerability and assessment of contamination in groundwater resources. At the same time data gathering, processing, geo-referencing, integration, aggregation, frequent monitoring, spatial analysis, and produced maps in accuracy and appropriate scales are much useful for local decision-makers (Lake et al., 2003; Wang and Yang, 2008). Besides, the area is screened and prepared where there is high pollution or less, vulnerable to pollution, thus preventing further pollution and more (Nolan et al., 2015; Rahman, 2008).

In the present study, different methods by GIS were performed. The Inverse Distance Weighting (IDW) interpolation technique was chosen for obtaining better results. The results of the spatial distribution of NO_3^- concentrations in the groundwater sources are shown in Fig. 4. The sources located in rural are represented with blue, and urban with pink color. The values of NO_3^- concentration were classified by size, less than 50 mg/L, 50–100 mg/L, and more than 100 mg/L.

Figures 5a and 5b are shown NO_3^- levels with the IDW technique. It is shown that the high level of NO_3^- was located in the western and central areas, while the low-level ones were in the southern and eastern areas. The high concentration of nitrate in these areas was possibly related to the bedrock sources and duration and frequency of rainfall (Enwright and Hudak, 2009). On the other hand, areas with high anthropogenic activities such as waste disposal sites, industrial estates, agriculture (which applies pesticides and fertilizers) are hazardous to groundwater. In a study, in the aquifer of Tunisia, it was shown that there was a high similarity between incorporates hydrogeological and hydrochemical datasets that revealed the more hazardous pollution zones and the areas with low water quality (Saidi et al. 2011).

Various studies reported a relationship between high NO_3^- concentration of groundwater resources and proximity to agricultural, industrial, and residential areas (Gao et al. 2012;Wongsanit et al. 2015;Lawniczak et al. 2016;Serio et al. 2018). In other words, using excessive fertilizer and moving pollution of stream water to groundwater, animal operation, wastewater disposal, industrial waste in this area can pollute groundwater. The land use map of the Isfahan area is shown in Fig. 6, as well water samples with NO_3^- concentration above 50 mg/L. Most of these samples are located in residential and agricultural areas. (Pardo-Igúzquiza et al. 2015) showed there were two very specific areas in the city of Granada, Southern Spain, where there is the probability of nitrate being higher than 100 mg/L. These two areas were located in the main urban and industrial areas and areas corresponding to intensive farming practices and sewage disposal. (Su et al. 2013) in the north china reported groundwater level of NO_3^- was high in the agricultural area and near wastewater draining canals. Also Chen et al. 2019 showed that agricultural sources and fertilizers were identified as the main sources of nitrate contamination both in wet and dry seasons (Chen et al. 2019). In Atlantic Canada, Liang et al. 2020 indicated land use was the dominant factor affecting nitrate load groundwater in growing and non-growing season (Liang et al. 2020). Besides, in a study (Cheong et al., 2012) in Korea reported samples with high nitrate concentration in groundwater located in agricultural land which was used sewage fertilizers. Also, they found a positive relation between NO_3^- concentration and radial distance of NO_3^- sources. Figure 7 shows the NO_3^- concentration in aquifers in the study area. As can be seen, Dahag (4204), Daran and Damane (4214), Najafabad (4206), Nayin (4806), and Tiran and Karvan(4207) aquifers, part of Ardestan (4801), Moute (4129), and Lenjanat (4209), have high NO_3^- concentration. It seems that issues such as agriculture, livestock waste dump pits, solid waste disposal, and poor sanitation, especially in rural areas, have reduced the quality of groundwater resources in the region (Reddy et al. 2011). (Blarasin et al. 2020) identified on-site sanitation systems and/or the animal pens in the urban area, while urea-based fertilizers and livestock breeding activities in the rural environment where the main sources nitrogen pollution. Results of a study in Russia/Ukraine showed that nitrate concentration was highly variable from 0.5 to 100 mg/L in groundwater, it was an additional indicator of manure and sewerage leaks in the shallow aquifer (Vystavna et al. 2017). Furthermore, in a study (Reddy et al. 2009) relation between the shallow and moderately deep aquifers and nitrate were observed by agriculture practices, sewerage, and organic waste disposal methods.

The water quality parameter maps (temperature, electrical conductivity, pH, and chloride ions) are shown in Fig. 8. The data in resources are classified by size symbols and shown by different colors in rural and urban areas. The temperature, which was between 5–34°C is shown in Fig. 8 (a). The pH was in the range of 6.2 to 8.7 and is also shown in Fig. 8 (b). Figure 8 (c) shows the EC variations between 110 and 16905 (μmhos/cm). The concentration of chloride ions in the samples was found to be in the range of 4 – 5284 mg/L, is shown in Fig. 8 (d). As can be seen in these figures, the studied parameters have more values in the central and east areas than the others which probably can be due to conditions such as geological characteristics of the soil, groundwater depth, topography, slope, hydrodynamic coefficient, etc. Statistical analysis showed that there was a low significant relationship between groundwater NO_3^- content and Cl^- ions in rural groundwater samples ($p < 0.001$ and $r = 0.169$) and was not significant in urban samples ($p = 0.848$). However, other parameters including EC, pH and temperature were significantly related in both urban and rural water samples ($p < 0.001$).

Heath risk assessment of nitrate

Nitrate is converted to nitrite and changed hemoglobin into methemoglobin in red blood cells. This is of concern in adults with diseases such as achlorhydria or atrophic gastritis. Furthermore, since the infant gastrointestinal system normally has a high pH; therefore, the risk posed to these age groups is much greater. Also, nitrite is formed via nitrate reduction in the human body that can react with secondary amines to form nitrosamines, which can be carcinogenic. Nitrate is a normal component of the human diet. If water containing high levels of nitrate (up to 10 mg nitrate-nitrogen/L) was consumed, the daily intake of nitrate could reach. The RfD of 1.6 mg nitrate-nitrogen/kg/day is based on the assumption that thresholds exist for certain toxic effects. In this study, the non-carcinogenic health risk of nitrate drinking groundwater was calculated as a daily Intake (EDI) and hazard quotation (HQ). EDI value was calculated for age groups (Table 1) of each sample. Mean, max, min, and standard deviation (S.D) for EDI of each group age are shown in Table 3. In this regard, the highest intake values of EDI in rural and urban areas were related to infants 4.98, 7.61; and children 1.56, 2.38, respectively. For infants, 284 samples in rural and 132 ones in urban area EDI values were above RFD (1.6 mg/kg.day). Also, 6 samples (children), 5 (male), and one in teens and females were high in urban. In the study (Thomson et al. 2007) daily intake of nitrate was 7 times more than the adult RFD.

Table 3
The EDI (mg nitrate-nitrogen/kg.day) values in infants, children, teens, male and female adults in the rural and urban area

Age groups	**Rural**				**Urban**			
	Mean	**S.D**	**Min**	**Max**	**Mean**	**S.D**	**Min**	**Max**
Infants	1.25	0.88	0.02	4.98	1.38	1.15	0.11	7.61
Children	0.39	0.27	0.01	1.56	0.43	0.36	0.03	2.38
Teens	0.26	0.18	0	1.04	0.29	0.24	0.02	1.58
Males	0.31	0.22	0	1.25	0.34	0.29	0.03	1.90
Females	0.27	0.19	0	1.07	0.30	0.25	0.02	1.63

In the present study, HQ value ranges of nitrate in drinking groundwater samples were for the infant (0.009–3.11), and (0.066–4.75), children (0.003–0.97), and (0.021–1.49), teens (0.002–0.65), and (0.014–0.99), male (0.002–0.78), and (0.016–1.19), and for female (0.002–0.67), and (0.014–1.02) in rural and urban areas, respectively. Notably, the HQ in urban areas was higher than the value obtained in rural areas in all of the groups. Furthermore, infants had the highest health risk, in 32% of samples, i.e. for the urban 136 samples and the rural areas 297 health risk value was greater than one (HQ > 1). Also, in urban areas, HQ was above one in 8, 5, 1, and 3 samples in children, teens, male and female, respectively. Besides, no relevant differences were observed between the group ages, although the risk was higher for the infants. Therefore, it could be inferred that there is a non-carcinogenic threat from the daily intake of drinking water in the infant population in some of the regions in Isfahan, while no non-carcinogenic risks were observed in the other groups. It is also notable that the estimated risks in infants were higher when compared to adults, which indicated that infants were more susceptible to the health risks associated with nitrate contamination. This finding is consistent with the studies in this regard, reporting that risk by nitrate contamination in infants is more significant compared to other populations since they consume more water per kilogram of their body weight and physiology. In a similar study, the health risks of nitrate in the groundwater in northwestern (semi-dry) China in infants, children, and adults were investigated. Results showed that the health risk of samples was in infant and children higher than adults. HQ is more than one for infants and children in 72% and 60% of the samples, respectively, and for men and women in 28% and 22% of cases, respectively, it is in the range of health risk (Chen et al. 2017). In another research, (Sadler et al. 2016) examined the health risks of nitrate in wells water in the rural areas of Indonesia. According to their findings, the risk index for infants was higher than adults, and HQ 50 and HQ 95 of infants were 0.42, and 1.2. Also, they showed with decrease NO_3^- level by health program, the risk of birth defect HQ50/50 decreased in later years. In a study conducted in Thailand, the risk of nitrate groundwater for children was in the range of 0.04–4.58, and for adults was 0.02–2.29 (Wongsanit et al. 2015). Besides, (Su et al. 2013) investigated the groundwater in the northern China and the associated health risks. They reported that in the study area, nitrate in 91.4% of the samples was about 34.3% above the standard level and drinking these groundwater containing high concentrations of nitrate was shown to be harmful to human health. Groundwater nitrate hazard was also reported to be higher near sewage canals and agricultural areas, while less was observed in urban areas. In addition, the health risk was lower in adults than in children. However, in the south Korea the hazard index (HI) of nitrate in groundwater was 0.75 (Cheong et al. 2012). In a study in northeastern China Teng et al. 2019 reported HI of nitrate for both adult and child in 46.4% parts of the area were larger than 1. Also children have a higher susceptibility of exposure to nitrate contaminants (Teng et al. 2019).

The spatial distribution of nitrate risk for methemoglobinemia in each sample of the study area groundwater is shown in Fig. 9. (a) Infants, b) Children, c) Teens, d) Males, and e) Females). As can be seen, the HQ values through ingestion exposure did not exceed the recommended values for children, teens, and adults while the value was higher than one for infants ($HQ > 1$) in some regions, especially, in the western and central region. In other words, the highest HQ value was belonging to Najafabad and Nayin cities. HQ values are consistent with NO_3^- concentration, therefore, high HQ in rural samples was in winter and low HQ occurred in the fall. Also, in urban samples, fall had the highest, however, the spring had the lowest ones ($p < 0.001$).

Conclusions

This study has indicated nitrate concentration in drinking groundwater resources and the health risk of respondents of Isfahan province, Iran. Results showed that nitrate levels ranged in rural samples 0.4-136.9 mg/l and urban ones 2.9-209.2 mg/l. In the study area, NO_3^- concentrations in 25% of samples were higher than the WHO or Iranian standard (50 mg/L) in some of the areas. NO_3^- levels were high in rainy seasons; high-level nitrate in the rural area was in winter and for the urban area was in fall. The maximum nitrate concentration was observed in the central and western areas of Isfahan province.

Spatial modeling of health risk from nitrate exposure using a probabilistic model was applied. The results of the health risk assessment indicated that the health risks exceeded the recommended levels for infants in some areas of the province, which could pose severe threats to their health. HQ of nitrate in infants was higher than one (HQ > 1), in 32% of samples (136 samples of urban and 297 samples for rural areas). Non-carcinogenic risks in infants were higher than when compared to the other groups. The HQ of NO_3^- in infants was greater than 1 in some counties, including Ardestan, Buyin, Dehagan, Falavarjan, Frydan, Fraydonshahr, Khansar, Kashan, Lenjan, Najafabad, Mobarake, Nayin, Natanz, Shahinshahr, and Tiran, where were the highest levels of NO_3^- contamination. Moreover, infants are a vulnerable population so that they are at a high risk of non-carcinogenic hazards from exposure to drinking water with high NO_3^- levels, which should be addressed. Water ingestion and body weight could be considered factors of uncertainly in risk estimations; the difference in body weight of individuals, weather conditions can greatly affect drinking water consumption. The consumption rate of drinking water in a hot climate is high. As a result, NO_3^- intake can be different. In the present study, only the drinking water exposure pathway was considered for the non-carcinogenic risk for Isfahan residents' exposure to NO_3^-. Other NO_3^- sources such as food and vegetables can significantly contribute to daily intake. Therefore, the level of risks from NO_3^- in Isfahan may be higher than the calculated values in this research. A monitoring program and health education should be in place in areas where drinking water has a high probability of nitrate contamination such as in agricultural areas. Specific regulations and the control of nitrate discharge are required to decrease the nitrate concentration in groundwater, water resources management is essential to avoid the growing contamination problem. Also, this study gives an overview of the drinking groundwater quality of the Isfahan Aquifer. This overview can form the basis for further investigations.

Declarations

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Consent for publication

This paper is a part of an approved MSc Thesis (#395894) at Isfahan University of Medical Sciences.

Availability of data and material

The authors confirm that the data supporting the findings of this study are available within the article.

Competing interests

The authors declare that they have no competing interests.

Ethics approval and consent to participate

Not applicable.

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Authors' contributions

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by [Saba Aghapour], [Mohammad Javad Tarrahi], [Fahimeh Amiri], and [Afshin Ebrahimi]. The first draft of the manuscript was written by [Saba Aghapour] and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Figures

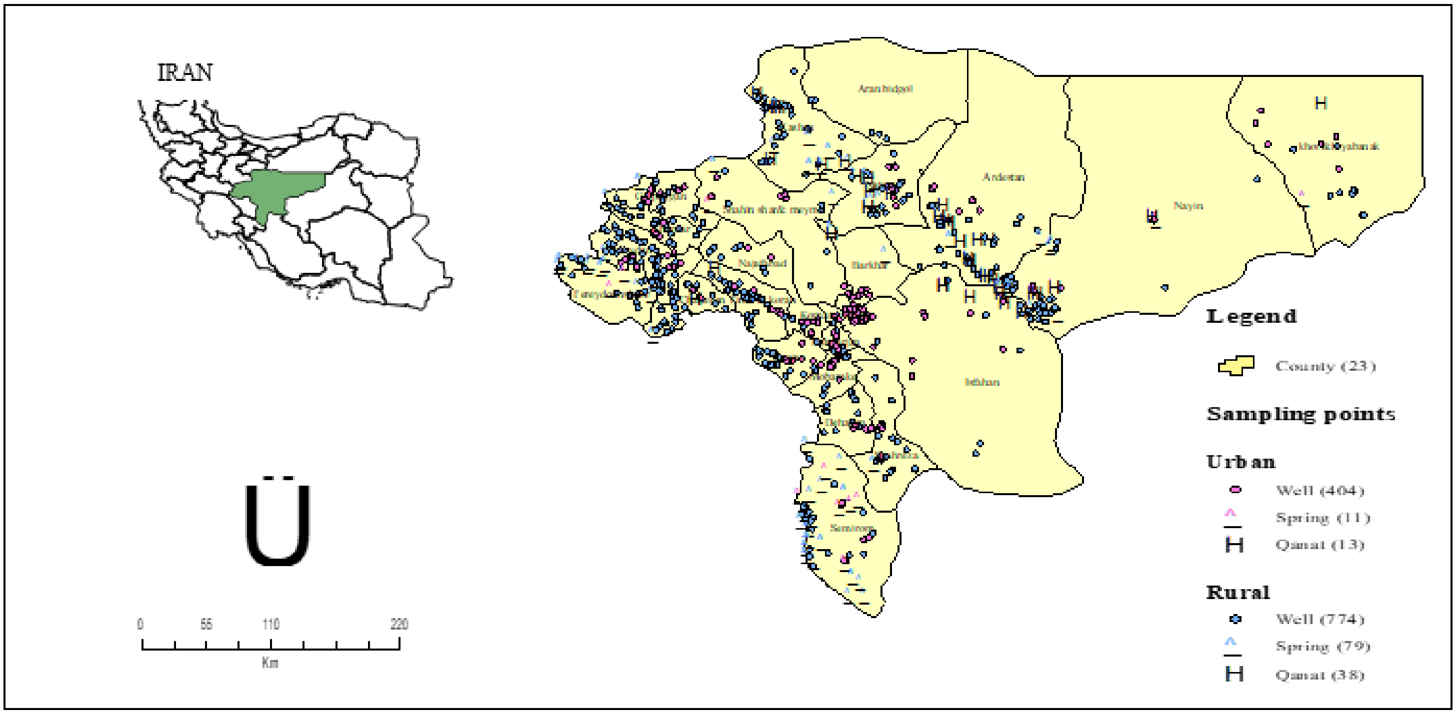

Figure 1

Location map of the study area and sampling stations

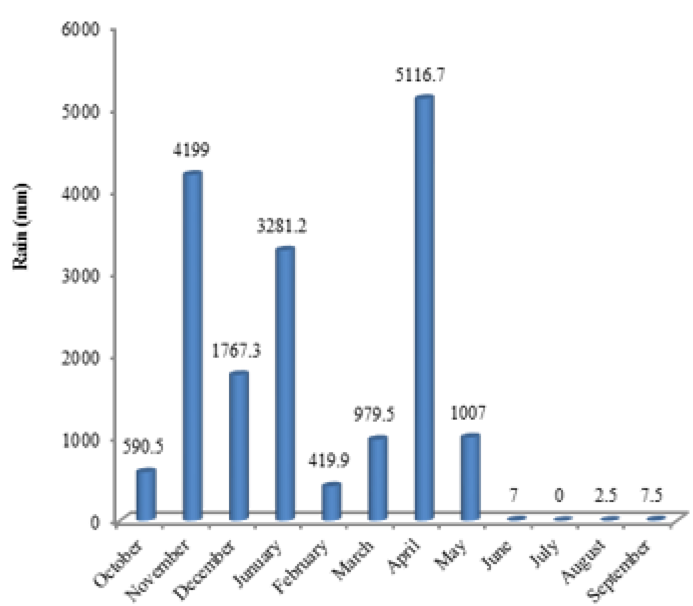

Figure 2

Rainfall in months of 2018 in Isfahan province

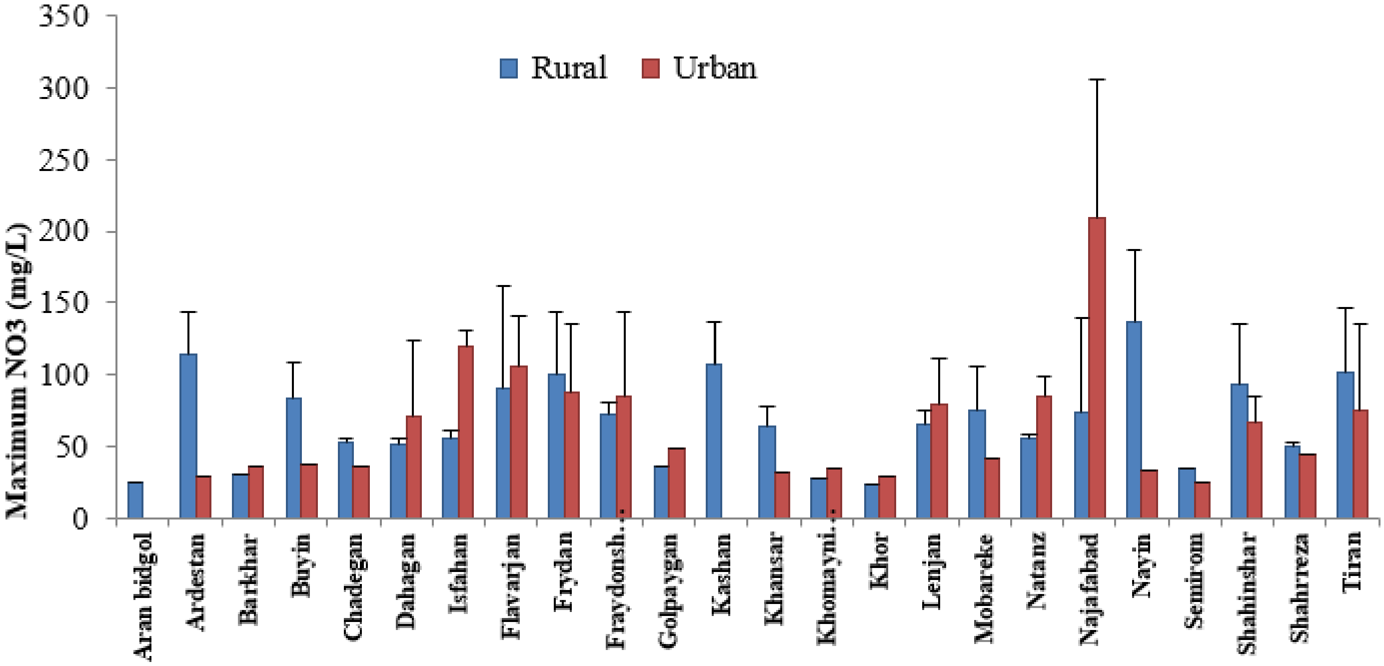

Figure 3

Maximum NO3- concentration of the samples in rural and urban area for each of county in the Isfahan province

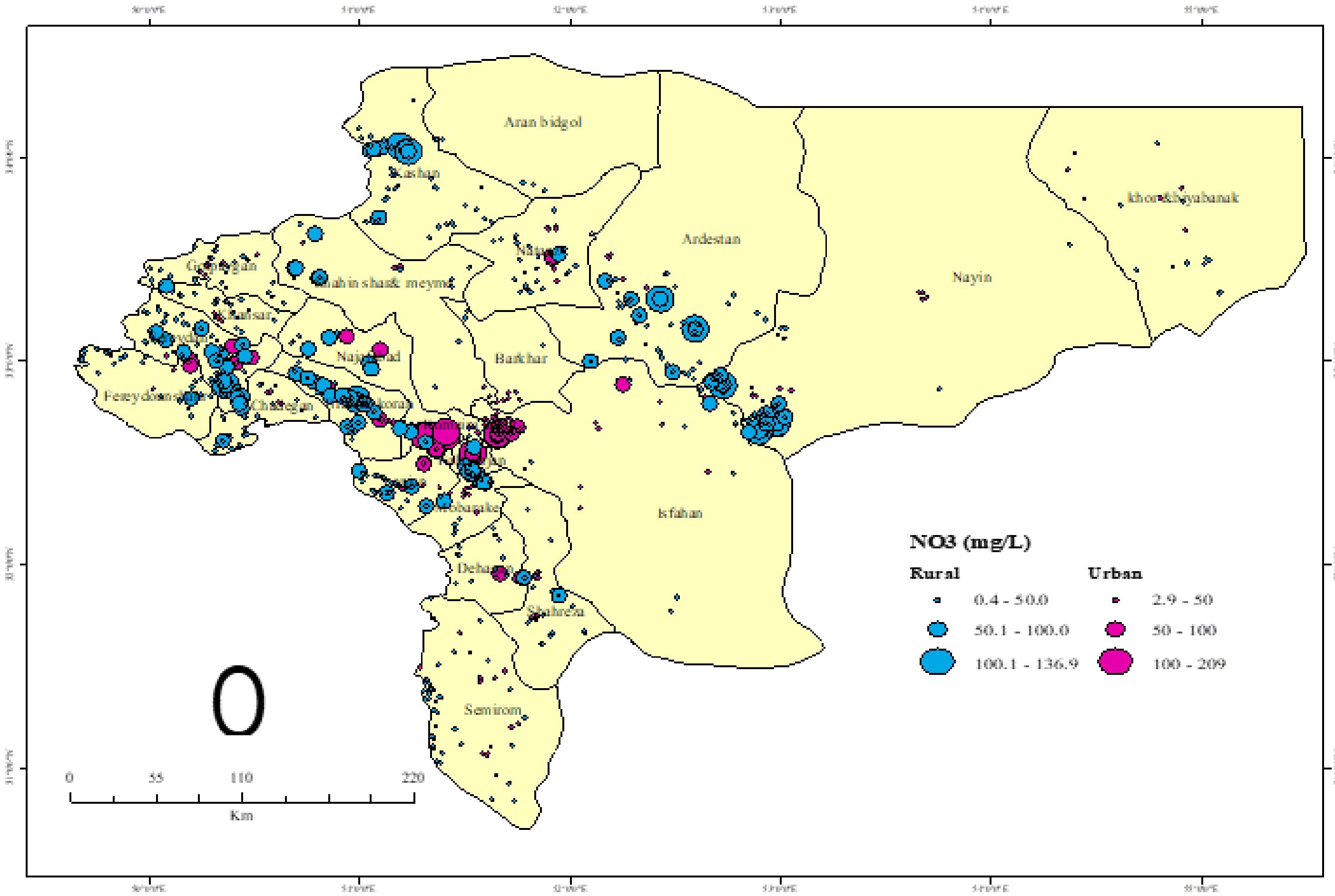

Figure 4

Spatial distribution maps of NO3 concentrations for each of the samples

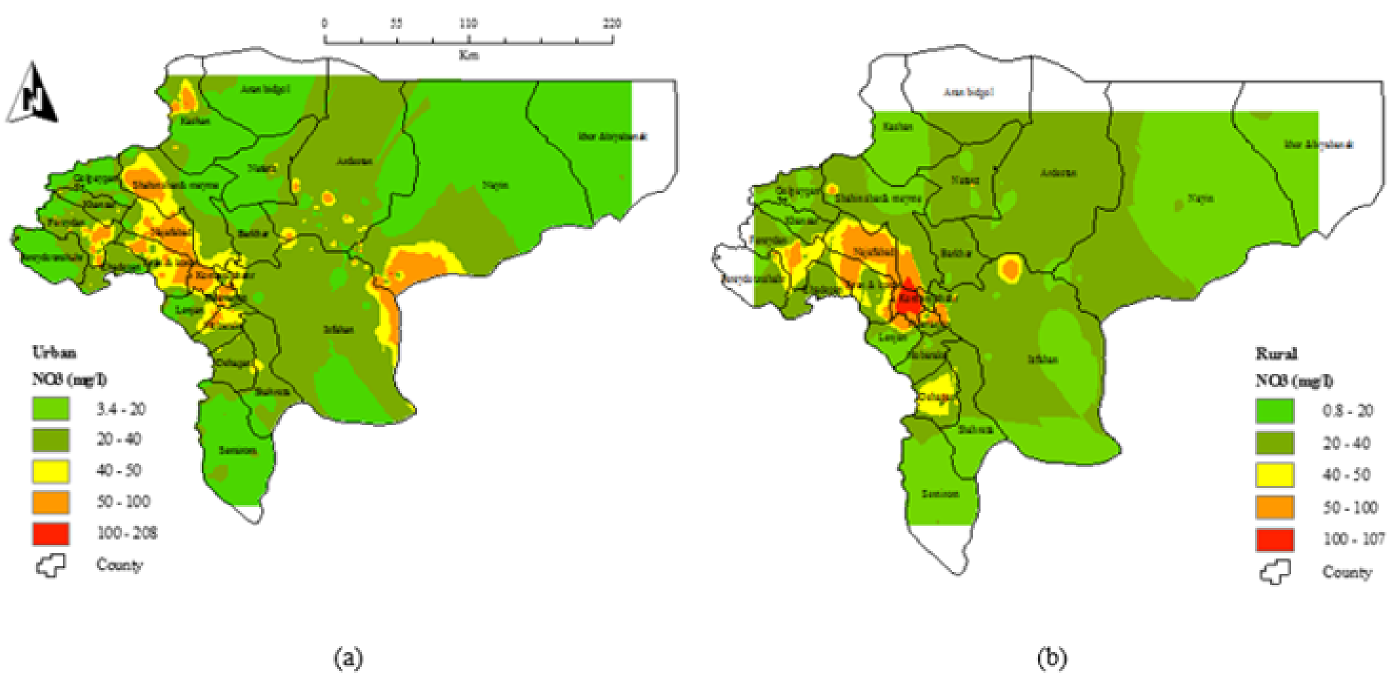

Figure 5

Spatial distribution of NO3 concentrations a) urban; b) rural areas

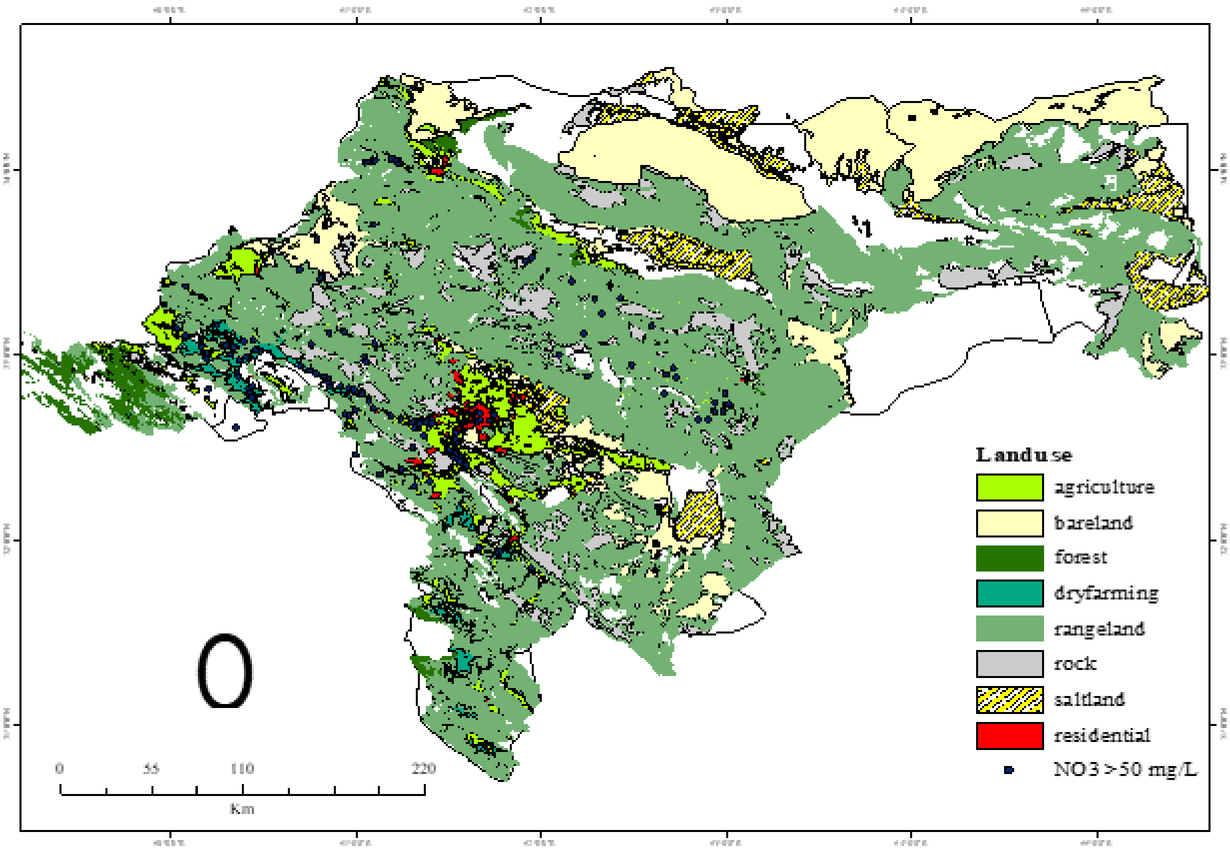

Figure 6

Land use map in Isfahan province and location of NO3 concentrations of the sample above 50 mg/ L

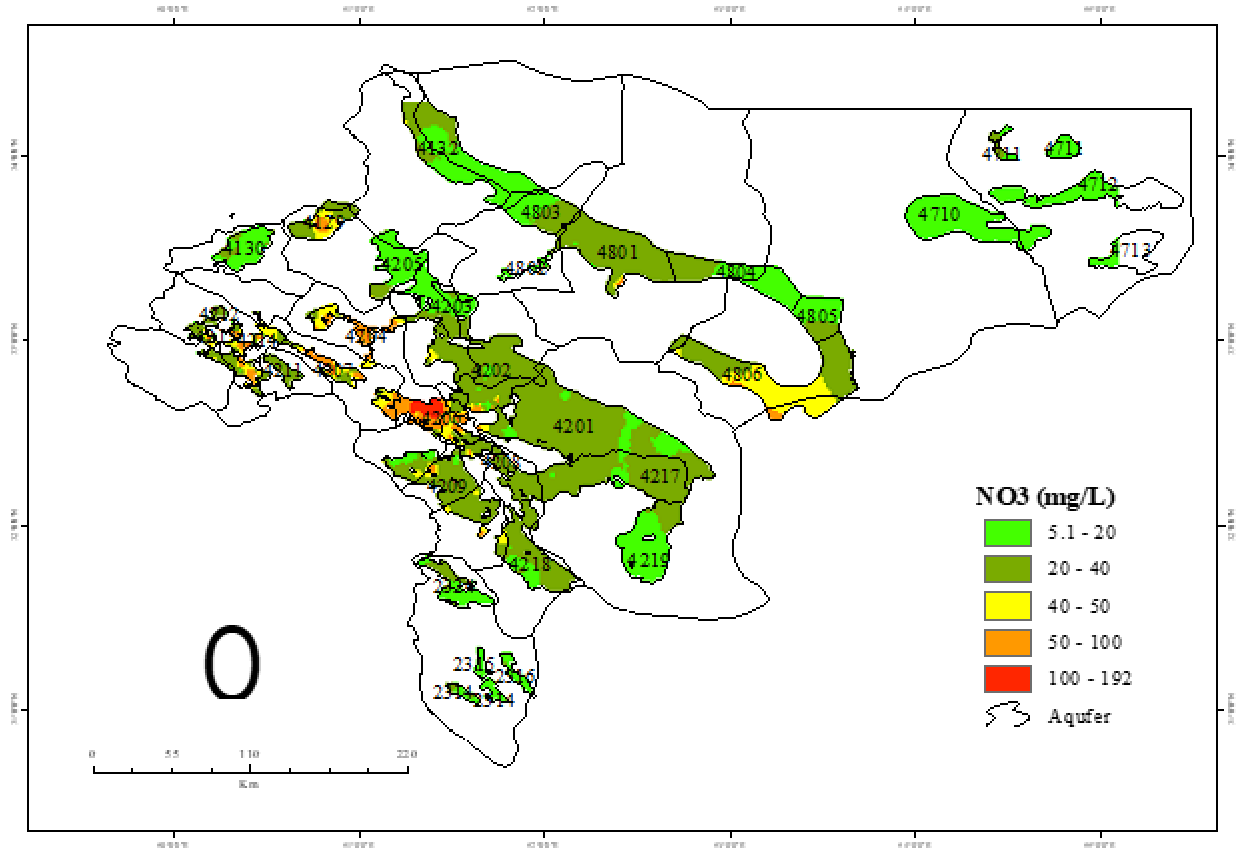

Figure 7

Spatial distribution maps of NO3 concentrations in the aquifers in Isfahan province

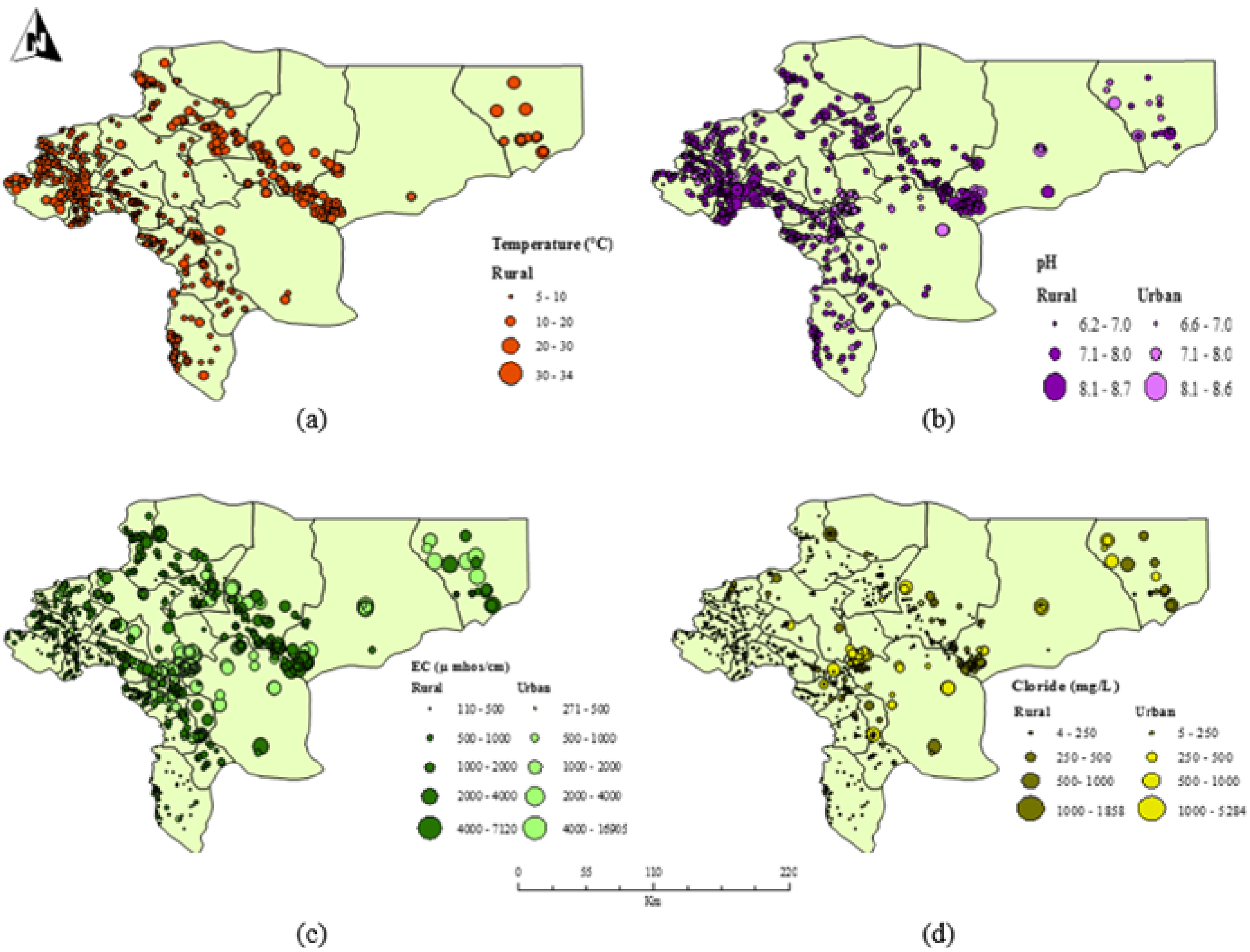

Figure 8

Spatial distribution maps for a) T°C, b) pH, c) EC, and d) Cl-

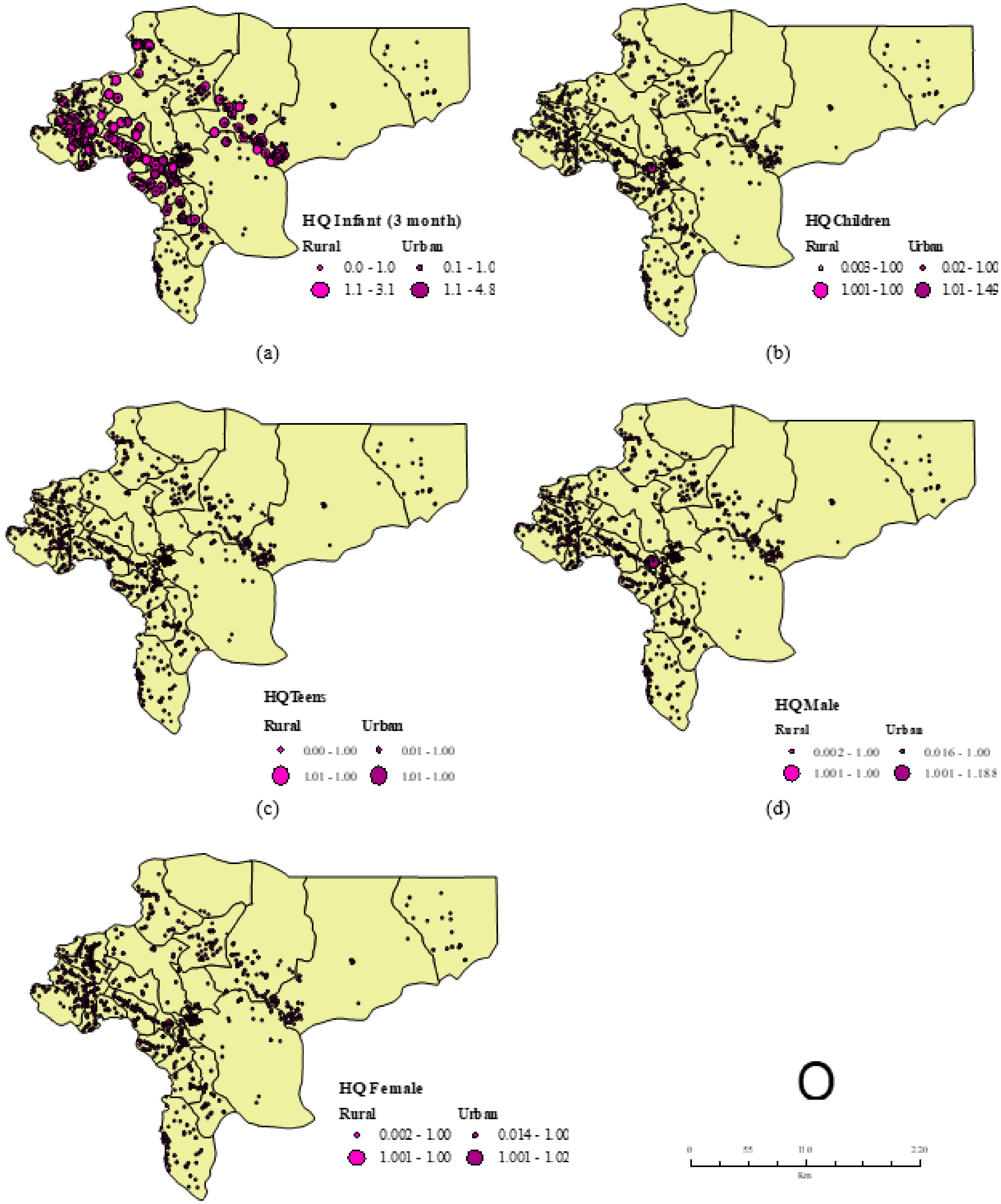

Figure 9

Spatial variation of HQ for different age groups: a) infants, b) Children, c) Teens, d) Males, and e) Females for each of the samples