Original Article

Determination of Nitrate Concentration in Groundwater in Agricultural Area in Babol County, Iran

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Abstract

Background and Purpose: Elevated nitrate concentrations in drinking water can cause methemoglobinemia in infants, stomach cancer in adults and nitrate poisoning in animals as well. Modeling of nitrate fate and transport in groundwater to minimize nitrate concentration in groundwater has been studied by numerous researchers.

Materials and Methods: In order to determine the potential nitrate and nitrite ions contamination of groundwater, 93 groundwater samples were collected. All the observation wells were located in agricultural areas. In order to measure the amount of nitrogen in the soil, 45 samples from the entire region were randomly selected and analyzed.

Results: The results showed that in 82% of groundwater samples nitrate concentration has exceeded the standard level of 10 mg/l as N. Water level in orchard fields were between 1m to 3.7 m below the ground surface. Nitrate concentration in all samples from the citrus orchard fell within the standard levels. Simulation of potential nitrate movement was performed in 4 different areas. Results indicated that in the rice field nitrate penetrated to the depth of 3.2 m that was the deepest nitrate seepage between four areas. Probable reasons of different results in these areas are discussed.

Conclusion: The simulated and observed measured data showed that the model was able to predict the groundwater quality changes within the soil profile and the aquifer.

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Key words: Groundwater, Contamination, Nitrate, Iran, Modeling

1. Introduction

Water contamination consists of physical, chemical or biological changes in water in a way that the water is not potable for human or usable for other purposes anymore. The contaminations would be the cause of water shortage for domestic, industrial, agricultural or any other demands. Availability of safe drinking-water that is one of the basic human rights is essential to health and also is a component of effective health protection policy (1). Existence of safe drinking water in rural areas is decreasing because of population growth which causes more water extraction from shallow groundwater, and increasing food production to cope with challenges in food demands, which causes a high use of agrochemicals (2). Agriculture is one of the human activities which have a serious impact on nitrate contamination of groundwater (3-5). Using nitrogen fertilizers and leakage of nitrate from livestock has decreased the groundwater quality (6). Previous studies indicated that there is a close relation between nitrate contamination in groundwater and operation of agricultural management (7-9).

High concentration of nitrate in drinking water can cause drastic diseases including methemoglobinemia in infants and stomach cancer in adults (8,10). A concentration of 10 mg/l is a generally accepted maximum for safe drinking water (11). WHO (World Health Organization) the guideline for drinking water proposed the standard levels of 10 mg/l for nitrate concentration in drinking water (1). US EPA (United State Environmental Protection Agency) maximum contaminant levels for nitrate and nitrite concentration in drinking water are 10 mg/l and 1 mg/l, respectively (11).

To control and hinder the nitrate contamination in shallow groundwater, effective management is necessary which needs extended studies. Many researchers studied groundwater contamination caused by nitrate and nitrite. For example, Chern etal. carried out a research in Wisconsin (12), his study showed that 10% of samples collected from 800,000 wells and 17-26% of wells in agricultural areas exceeded the limit of 10 mg/l (threshold suggested by US EPA). Thorburn et al. conducted an investigation in intensive agricultural areas of northeast Australia (13). This research is carried out using N^{15} techniques and showed that 14-21% of wells were contaminated by nitrate which about 50% of these contaminated samples source of contamination was N fertilizers. Wick et al. found that there is a positive correlation between the percentage of croplands in a given region and nitrate concentration in groundwater (14). According to their research environmental characteristics such as temperature and precipitation are important co-factors; higher average temperatures causes less nitrate contamination of groundwater- possibly due to increased evapotranspiration- and higher average precipitation ends to reduction of groundwater nitrate concentration. Researcher tried to collect groundwater samples monthly during 1997-1999 from 20 wells to evaluate the nitrate contamination source of unconfined groundwater in the North Han River basin (15). They reported that 43.9% of samples exceeded the national standard for drinking water (10 mg/l). Nitrate concentration in this area increased with direction of groundwater flow and denitrification was not observed because of the coarse texture of soil matrix so this study suggested reducing the nitrogen inputs through curtailment of fertilizer and compost application rates and appropriate treatment of livestock manure for preventing groundwater contamination.

Some researchers have carried out in north of Iran to determine the amount of nitrate concentration in soil, surface and shallow ground water. In 1995, sampling from surface and groundwater including water in rice fields, rivers, drains, domestic wells and semi deep wells were done in Gilan and Mazandaran provinces, Iran. Results showed that the most nitrate fluctuations were related to domestic wells. In the wet season 13% of samples and in a dry season 3% of them had the concentration, which exceeded the standard level of 10 mg/l (16). According to measurements of nitrate in Haraz River in July 2000, concentrations at in the beginning of the river and in the end of that (sea coast) were 1.1 mg/l and 2.3 mg/l respectively. This value was 3.2 mg/l in rice field outlet. All these values fall within the US EPA standards (16).

2. Materials and Methods

Babol is located in Mazandaran province, Iran. This area encompasses 14301 km^2 which is about 5.94 percent of the Mazandaran province, is located between 36° 05' and 36° 35' latitude, and 52° 30' and 52° 45' longitude. City of Babol is situated 210km northeast of Tehran and it is surrounded by Babolsar at north, Alborz Mountains at south, Amol city at west and Ghaemshahr and Savadkooh at east. In this area, main source for drinking water supply is shallow wells. A well is considered to be shallow if it is <50 feet deep. It is clear that the source of a well is an aquifer.

The maximum water table depth is at 5.5 m level in the southern part of plain, and the minimum is at the level of the ground surface; however, the average depth is 2.5 m. The observed data shows groundwater hydraulic gradient and flow directions are from the east to the west of the region. About 6% of this area (809 km^2) is under cultivation of rice, citrus, fresh vegetables, melons, cereal and other products.

The main nitrogen fertilizer used in this region is urea fertilizer (17). Solubility of urea is very high and in rice cultivation any amount of this fertilizer added to soil, is washed away rapidly and could add to the groundwater. Dissolved nitrogen finally converts to nitrate and causes a variety of diseases especially in children. Two major types of fertilizers are used in Babol; urea and phosphate fertilizer which are used in the amount of 13000 tons and 4000 tons, respectively (18).

Annual average amount of fertilizers used for different crops is shown in table 1. Table 2 shows the properties of three most dominant soil type in study area in different layers. Amount of precipitation and evapotranspiration in this area was measured

Table 1. Annual amount of fertilizer used in different cultivation Babol city (kg/ha) (18,19)

Type of cultivation	Use of urea fertilizer (Kg/Ha)	Phosphate fertilizer (Kg/Ha)
Rice	200	50
Citrus	100	50
Summer crops	150	Nil
Cereal	150	50
Other	100	50

Table 2. Soil analysis of three most dominant soil type in study area (17-19)

Soil nam	Horizon	Depth (m)	Organic carbon (%)	Bulk density (g/cm^3)	Volumetric water content (%) at −0.01	at −15 Mpa	Saturation
Babol	1	0.15	2.4	1.35	40	12	46
	2	0.45	1.44	1.35	40	12	50
	3	0.8	0.86	1.35	40	12	50
	4	1.3	0.6	1.4	40	10	50
Darzikola	1	0.15	1.9	1.35	40	12	50
	2	0.65	0.87	1.2	40	14	50
	3	0.95	0.9	1.2	40	14	50
	4	1.2	0.7	1.35	40	10	50
	5	1.5	0.3	1.35	40	10	50
Haraz	1	0.22	0.74	1.3	35	15	44
	2	0.64	0.62	1.35	35	15	44
	3	1.12	0.35	1.35	35	15	44
	4	1.5	0.32	1.3	35	15	44

Table 3. Average 3 years hydrological data of the study area

Month	2009		2010		2011	
	P (mm)	ET (mm)	P (mm)	ET (mm)	P (mm)	ET (mm)
1	38.9	30.2	1.1	34.4	22.6	24.7
2	24.8	42.4	2.6	48.6	13.5	39.1
3	196.3	17.1	40.3	19.1	117.4	18.3
4	204.4	76.1	281.3	80.9	241.3	73.6
5	181.1	162.6	197.8	173.4	200.7	181.4
6	270.5	239.2	280.5	248.8	306.0	220.8
7	193.7	89.2	187.8	88.0	132.0	82.5
8	4.4	23.1	8.2	23.5	38.9	22.4
9	74.1	16.2	39.6	16.7	42.4	15.2
10	23.0	10.7	80.1	9.4	30.2	9.1
11	11.0	46.5	9.1	49.4	25.3	38.6
12	17.0	37.2	18.0	33.4	18.5	22.4

water authority of Mazandaran. Available data of precipitation and evapotranspiration in study area are shown in table 3.

Since the purpose of this research was to investigate the shallow groundwater contamination due to the use of nitrogen fertilizer, efforts were made to minimize the effects of other contamination sources. From a list of 145 wells in the study area 93 well were selected randomly, so a uniform grid at the scale of 1 km × 1 km were made and adapted to the wells map. The selected wells were out of the residential area and mostly in agricultural zones.

Autumn was the season to start the sampling for three continues years. Extended researches and studies show that autumn could be the best season for sampling after a dry season because all the used fertilizer are completely washed out from the soil and is after harvest time. In this area there is no new second cultivation so all the nitrogen would be washed away and leached into the groundwater. A total number of 93 wells were selected for sampling purposes and water samples at different depths at seasonal intervals were collected and analyzed for nitrate and nitrite concentrations from 2009 to 2011.

Water samples analysis were performed using a DR2000 device in health department of Babol medical center. Nitrate concentration in 82% of samples exceeded the US EPA standard, but nitrite concentration in all samples fell within the US EPA standards. None of the samples in citrus cultivation area exceeded the standard limit; however nitrate concentration in all samples from rice field were higher than the standard limit. Average nitrate and nitrite concentration in all samples were 20.3 mg/l and 0.12 mg/l, respectively. Numbers of wells in each range of concentration are shown in table 4.

Table 4. Number of wells in each concentration range and percentage

Concentration range nitrate mg/l	Number of samples in the range	Percentage of samples in the range
0-5	4	4.30
5-10	13	13.98
10-15	15	16.13
15-20	19	20.43
20-30	26	27.96
30-40	7	7.53
40-50	9	9.68

2.1. Numerical transport modeling

There are several models to simulate chemical movement in soil. CHEMFLO was written to help perceiving of the flow and chemical transport system. New version of this software expands on that of Nofziger et al. by providing a graphical user friendly interface (20). The software solves mathematical model of water and chemical movement system which is defined by the user (21). LEACHM is the other model, which was used for predicting contamination transport in soil (22). The model was developed by Hutson and Wagenet (23).

Chemical movement in layered soil (CMLS) was developed to serve as a management and a decision making tool for simulation of organic chemicals movement into soils (24). Graphical outputs of the model show the effects of soil characteristics, chemicals and hydrological factors on chemical movement through the soil. This method makes possible to assess the potential contamination of ground water (25). CMLS has the advantages of: (1) Accuracy in the prediction of chemical movement; (2) Small simulation time requirement; (3) Minimum input value requirement; (4) Easy accessibility of the model output (26). Due to this advantages and availability of data which were matched with CMLS model input, this software was chosen for modeling purposes in this investigation. This model can calculate the penetration depth of chemicals into soil. Complex path of chemicals into soil is affected by soil factors like: pH, bulk density, field capacity, permanent wilting point, volumetric water content, and soil organic carbon content, which are evaluated according to FAO guideline (24). Chemicals properties including partition coefficient, degradation half-life, retardation coefficient, and climate and agricultural factors such as rooting depth of plants, precipitation and evapotranspiration will affect the result of modeling (27).

CMLS model which is used to estimate the chemicals movement in layered soil is the modified version of another model which was developed by Rao, Davidson and Hammond (28). It estimates the depth of the center of mass of a non-polar chemical as a function of time after application. In this model, chemicals move just in liquid phase in response to water movement in soil. The soil profile can be divided into 20 layers with different properties in each layer. Soil and chemical properties are uniform within a layer (29). Following equation represents the depth of chemical at time t+dt:

$$D_c(t + dt) = D_c(t) + \frac{q}{R\theta_{FC}} \qquad (1)$$

Where θ_{FC} is the volumetric water content of the soil at “field capacity” and R is the retardation factor for the chemical in the current layer of the soil. The retardation factor is given by:

$$R = 1 + \frac{\rho K_d}{\theta_{fc}} \qquad (2)$$

Where ρ is the bulk density of the soil and K_d is the partition coefficient or linear sorption coefficient of the chemical in the soil. Equation 3 assumes the sorption process can be described by the linear, reversible, equilibrium sorption model. Soil properties obtained from data samples and evapotranspiration and precipitation amounts data, which are measured and provided by Mazandaran Water Organization are used as input data for CMLS model (http://www.weather.ir).

3. Results

Regarding to depth of groundwater status, cultivated lands in the project are divided to four areas: Area 1; is the center part of the study area, most of this part are swamplands and like area 2 texture of soil is heavy and fine, which causes high water table depth about 1-2 m. In this area, fields are under rice cultivation and hence the usage of nitrogen fertilizer is higher than other areas. The laboratory analyses show high average nitrate concentration (About 17.74 mg/l in 27 observation wells in this area). Results showed that the nitrate concentration in all samples from wells located in rice fields were exceeded the standard level for drinking water.

Area 2; which includes eastern part of the study area contains fine and heavy textured soil, and water table depth is about 2-4 m. Average nitrate concentration obtained from testing 29 wells samples is 23.05 mg/l. Higher concentration of nitrate comparing to area 1 is because of shallower water table depth and also more nitrogen fertilizer use in the rice fields.

Area 3; which includes western part of the study area. In this area static water table depth is relatively deep and is about 4-5.5 m below the ground surface. During testes which performed in 19 wells, the average concentration of nitrate was 13.21 mg/l. The reason could be light-textured soils that hold lower water content. This area is under citrus cultivation that uses relatively less nitrogen fertilizer.

Area 4; is located at the southern part of the study area. Groundwater table in this area is relatively deep. Most of these orchard fields are located in areas with high surface elevations. Average nitrate concentration in 18 observation wells in this area (Area 4) was about 5.94 mg/lit which fell between the standard levels. This low concentration was because of low water table caused by light and coarse texture soil which holds less water contents. A summary of average nitrate concentration in water samples from different areas are shown in table 5.

CMLS model were performed in four different areas for 3 years (1095 days) in the period of 2009-2011. Results showed that parameters like amount and frequency of irrigation, precipitation, water table and soil texture are affecting the nitrate penetration depth.

Nitrate had the deepest penetration of 3.2 m in Babol rice field 1, between other places in the modeling areas. Large amount of urea fertilizer use and continuous irrigation are the main reasons. Between citrus orchards, highest amount of nitrate penetration depth happened in Haraz. Nitrate had reached the depth of the 2.2 m in this area. Nitrate in Darzikola citrus orchard had reached the depth of 1.9m; this amount is less than Haraz, because soil texture was lighter in Haraz (Figures 1 and 2).

Table 5. Average nitrate concentration in samples from different areas

Area	Number of wells	Average (Min, Max) Nitrate concentration mg/l, as NO3
Rice field 1 (Babol)	27	17.74 (45.7, 11.9)
Rice field 2 (Babol)	29	23.05 (45.5, 14.3)
Citrus orchard 3 (Haraz)	19	13.21 (28.2, 7.2)
Citrus orchard 4 (Darzikola)	18	5.94 (25.5, 4.3)

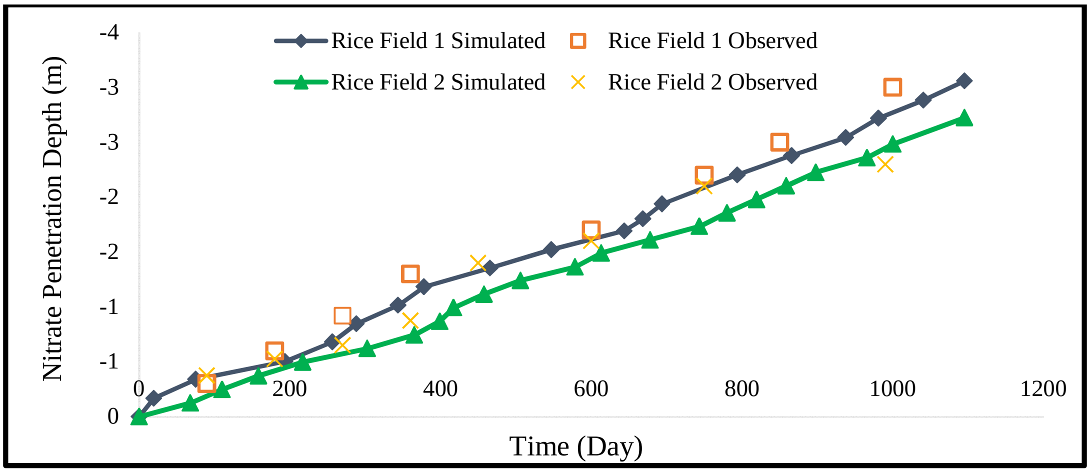

Figure 1. Nitrate penetration depth in Babol rice field 1 and field 2

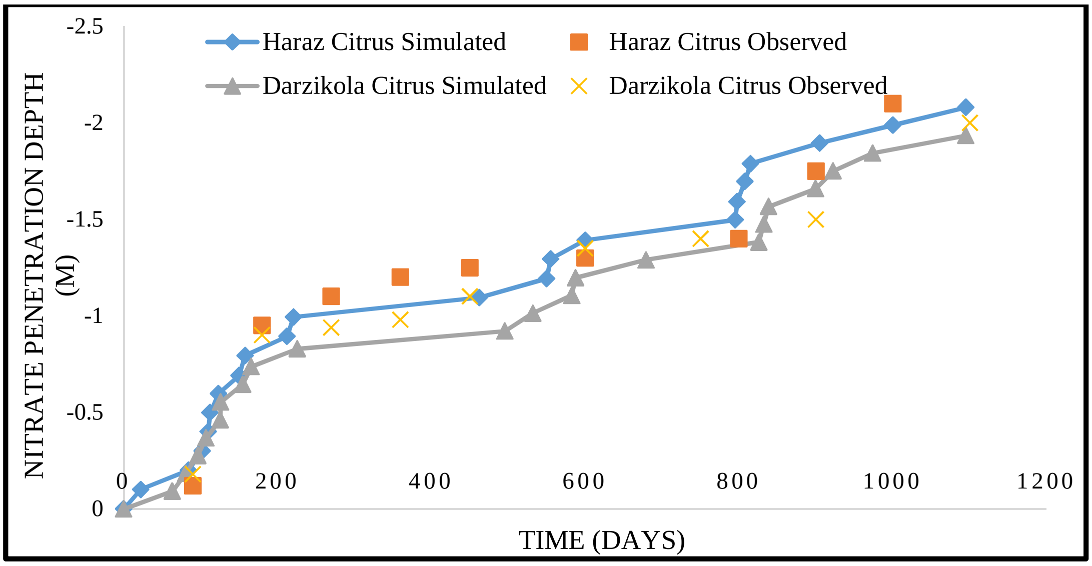

Figure 2. Nitrate penetration depth in Haraz Citrus and Darzikola Citrus

In several previous studies, it has been demonstrated that nitrate nitrogen (NO−3 −N) is the most frequently entering groundwater causing pollutant (30-32). The studies show nitrate concentration of groundwater depends on its influencing local hydro-geology factors and human's cultural behaviors (33,34).

4. Discussion

Nitrate depth in citrus orchard areas were considerably less than rice field because of less irrigation, less fertilizer use and lower water table in these areas. Nitrate seepage rate in citrus orchard in Haraz, and Darzikola citrus orchard was higher in 1st year due to high precipitation in the areas in 1st year. However results had not the same trend in Babol rice fields. In Babol rice fields seepage had a uniform trend. The reason of this manner is continuously use of nitrate fertilizer and irrigation, which makes the field completely saturated all the time.

As the precipitation decreases in next 2 years of the study period, penetration rate of nitrate in soil decreases as well, in citrus orchard in Haraz and Darzikola citrus orchard. However, again in Babol rice fileds, nitrate penetration rate remains constant, approximately. Nitrate seepage rate had the higher amount in wet seasons in all figures except figures 2 which had the step wise seepage rate. Simulations results show a good agreement with measured data. It shows nitrate contamination, which exist in our sampling data which is shown within the figures as simulated and observed data. Table 6 shows statistical analysis of simulated and observed data.

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Table 6. Statistical analyses of observed and simulated data

Area	RSQ	CD	RMSE
Babol rice field 1	0.93	0.91	17.50
Babol rice field 2	0.91	0.94	19.50
Haraz citrus	0.98	1.09	15.27
Darzikola citrus	0.91	0.94	19.50

RMSE: Root mean square error, CD: Coefficient of determination, RSQ: Correlation Coefficient

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