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To cite this article: Peng Li et al 2018 IOP Conf. Ser.: Mater. Sci. Eng. 452 022164

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The Nitrate Nitrogen in Groundwater of Intensive Agricultural Region in Pinggu District by Sampling and Monitoring for 12 Years

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Abstract. The nitrate nitrogen of groundwater samples which sampled 24 times from 2006 to 2017 in the intensive agricultural region of Pinggu district in Beijing were analyzed in this study, in order to investigate its dynamic change and important influence factors of this region. The results indicated that the mean value of nitrate nitrogen in groundwater of this region was 6.23 mg/L, which had reached the third level of the national groundwater quality standard, and the annual nitrate nitrogen concentration in groundwater of the region tended to increase. The significant positive correlations between the annual average concentrations of nitrate nitrogen in groundwater and the statistical data of livestock and poultry products from 2006 to 2015 implied that the impact of livestock and poultry industry on the nitrate in groundwater should not be ignored in the region. The increase of precipitation has a trend of increasing the difference of nitrate in groundwater in Pinggu district. The nitrate nitrogen in groundwater sampled from orchard was markedly higher than which from grain field and vegetable field. Samples from deeper well (WD3) always located in mountainous area, their nitrate nitrogen was significantly higher than which from spring well (WD1) and well with 30 to 100 m depth (WD2).

1. Introduction

Groundwater accounted for a proportion of 68\% of freshwater that could be used by human consumption in the world [1]. As the availability of surface water resources declines and more surface water is contaminated, people rely increasingly on groundwater for their drinking water. However, recent research [2-5] has shown that groundwater in many places has been contaminated by various contaminants, such as nitrate. Reports show that in USA, Canada, Japan, Europe, Australia and China the concentration of nitrate nitrogen in groundwater has been increasing [6-11]. There are some close relationships between groundwater pollution and human health condition. If the groundwater high in nitrate nitrogen was used for human consumption it may increase the risks developing methemoglobinemia and canceration of alimentary system [12]. As a result, many countries and organizations in the world have ruled the nitrate concentration criterion of groundwater quality in the drinking water. Groundwater is very important to Beijing as one of the water-scarce big city in arid and semiarid region. Pinggu district is located in the northeast of Beijing. The groundwater source
condition is good in Pinggu district and is one of the important emergency groundwater source for Beijing. Nearly 80 million m$^3$ of water had been supplied to the central city area each year from 2004 to 2014, which played an important role in ensuring the safety of water supply in the capital. The planting area for orchard was 17822.5 hm$^2$ in Pinggu district in 2016 [13], which accounted for 33.9% of that in Beijing and produced 49.0% of total yield of fresh fruit. Pinggu district is one of the important region in agricultural production in Beijing, where texture of most soil is mostly sandy and permeable. It resulted in many risks for nitrate pollution in groundwater. The investigation of nitrate nitrogen in groundwater of intensive agricultural region in Pinggu district was very important and should be performed for rational utilization and protection of water resource and security prevention of drinking water.

2. Material and methods

The intensive agricultural region in Pinggu district is divided into grain field, orchard and vegetable field according to the agricultural characteristics of this region. Groundwater samples were collected from a certain amount of irrigation wells which were selected from the region. The nitrate nitrogen of sampled water was tested after that. From year 2006 to 2017 there were totally 475 groundwater samples (Table 1) collected before (May) and after (October) the rainy reason annually.

| Sampling time | 2006 | 2007 | 2008 | 2009 | 2010 | 2011 | 2012 | 2013 | 2014 | 2015 | 2016 | 2017 |
|---------------|------|------|------|------|------|------|------|------|------|------|------|------|
| Orchard       | 19   | 40   | 40   | 40   | 40   | 40   | 40   | 40   | 40   | 40   | 40   | 40   |
| Vegetable Field | 11   | 10   | 10   | 10   | 9    | 10   | 10   | 11   | 10   | 10   | 10   | 11   |
| Grain Field   | 18   | 28   | 28   | 28   | 9    | 28   | 28   | 28   | 28   | 28   | 28   | 28   |

Before collecting a water sample, the sample container was washed at least 3 times by the sampling water. The water was dropped for several minutes before collected from a pump well or a hand-pump well. All samples were dissolved with 4 mL HCl (1:1) to ensure that their chemical component would not be affected by microorganism, and then taken to the laboratory to test the nitrate nitrogen by ultraviolet spectrophotometry [14].

3. Results and discussion

3.1. Temporal variation of nitrate nitrogen in groundwater

The range of average concentrations of nitrate nitrogen in groundwater for each sampling time from 2005 to 2017 in Pinggu district was from 0.01 mg/L to 105.39 mg/L, and the mean value of nitrate nitrogen of all samples is 6.23 mg/L which makes the water quality reach the third level of the national groundwater quality standard. The nitrate nitrogen in groundwater of this district was almost on a stable curve before 2011 while it was on the rise after that then (Fig 1). Before the year of 2011 the annual average concentrations of nitrate nitrogen in groundwater were from 3.5 to 6.0 mg/L, while after the year of 2011 they rose above 7.00 mg/L. The annual average concentration of nitrate nitrogen in groundwater of year 2017 was the highest of them all. It can be known that the gross output value of agriculture (GOVoAg) in Pinggu district had increased year by year from 1.87 billion to 4.67 billion (Table 2) [13]. As the correlation analysis result showed (Table 3), there were very significant positive correlation between GOVoAg and the number of farming employee, the output of pork beef and lamb (Output of PBL) and the output of eggs. In Pinggu district the livestock and poultry industry played an important role in producing value in the agricultural industry development. In such a circumstance, it also showed the significant positive correlation between the annual average concentrations of nitrate nitrogen in groundwater and GOVoAg, the number of farming employee, the Output of PBL and the output of eggs (Table 3). Questions whether the livestock and poultry industry had an impact on nitrate nitrogen in groundwater in Pinggu had been answered.
Figure 1. Mean values and C•Vs of groundwater nitrate nitrogen in different sampling times from 2005 to 2017.

Table 2. Gross output value of agriculture in Pinggu district from 2006 to 2015.

| Year | 2006 | 2007 | 2008 | 2009 | 2010 | 2011 | 2012 | 2013 | 2014 | 2015 |
|------|------|------|------|------|------|------|------|------|------|------|
| GOV of Agr (Billion RMB) | 1.87 | 2.17 | 2.51 | 2.64 | 2.94 | 3.44 | 3.97 | 4.47 | 4.82 | 4.67 |

Table 3. Pearson correlation between annual average concentrations of nitrate nitrogen in groundwater and different statistical data of Pinggu district from 2006 to 2015.

| Item       | Number of farming employee | GOV of Agr | Output of PBL | Output of eggs |
|------------|----------------------------|------------|---------------|----------------|
| AnNON      | 0.640*                     | 0.663*     | 0.724*        | 0.729*         |
| GOV of Agr | 0.960**                    | /          | 0.915**       | 0.844**        |

* Correlation is significant at the 0.05 level (2-tailed).
** Correlation is significant at the 0.01 level (2-tailed).

The coefficient variations (C•V) of nitrate nitrogen from 2006 to 2012 had a rising trend on the whole (Fig 1 and Fig 2). After the year of 2012, C•Vs of nitrate nitrogen in groundwater dropped from 197.3% to 126.0% and went steadily afterwards. The accumulated annual precipitation data from 2006 to 2015 measured by a rainfall station near this district was shown in Fig 2. It could be seen that the variation trend of the accumulated annual precipitation of this region was almost the same as that of the C•V of nitrate nitrogen from 2006 to 2015. After a correlation analysis was made it was concluded that there was a significant positive correlation (significant at the 0.05 level) between the C•Vs of nitrate nitrogen calculated annually and the accumulated annual precipitation from 2006 to 2015. The close positive relationship with the Pearson correlation of 0.712 was implied that the difference of nitrate nitrogen in groundwater from different sampling sites in Pinggu district was getting bigger when the precipitation increased meanwhile. The soil in Pinggu district is mostly sandy and permeable. The research area where samples collected includes flatlands, mountainous region and where they borders. The atmospheric precipitation infiltration was the important recharge of groundwater in both mountainous region and flatlands [15]. The hydrogeologic condition and flow recharge feature of this region were some of the reasons why there was a close correlation between C•V of nitrate nitrogen calculated annually and the accumulated annual precipitation.
Most of samples in the research area which were accounted for 95.5% with the nitrate nitrogen in groundwater lower than 20.00 mg/L (Fig 3). The samples which had nitrate nitrogen lower than 20.00 mg/L were accounted for 95.0% to 100.0% proportion of all from 2006 to 2013. The proportion of samples higher than 5.00 mg/L decreased since the year 2006 to 2010 and increased after 2010 till 2017. The proportions of samples higher than 20.00 mg/L, which were no more than 5.0% before 2014, increased to more than 6.0% since 2014. It implied that the nitrate nitrogen in groundwater of the monitored region had the rising trend in recent years, which also could be obtained by the vairation of annual average concentrations of nitrate nitrogen in groundwater (Fig 1).

3.2. The nitrate nitrogen characteristic of different agricultural land use
The results obtained from our investigation in according with 3 agricultural land use types showed that the average concentration of nitrate nitrogen in groundwater sampled from grain field, vegetable field and orchard were 4.14 mg/L, 4.03 mg/L and 7.74 mg/L respectively (Fig 4). The variance analysis showed that the nitrate nitrogen in groundwater sampled from orchard was markedly higher than which from grain field and vegetable field, while the nitrate nitrogen in groundwater sampled from grain field and vegetable field were nearly equal to each other. Mean depths of the wells where
groundwater sampled from grain field, vegetable field and orchard were respectively 91.3 m, 85.9 m and 148.1 m. They were significantly different from one another (Fig 4). Samples collected from wells within the orchard were usually located in the hilly regions or river valley and flatlands near the hill [16]. The groundwater under mountainous area is dominated by karst fissure water and its recharge mainly comes from atmospheric precipitation infiltration. The flatlands is an alluvial-diluvial fan, with a gradual thinning of sedimentary thickness from the mountain front to the center of the basin. The sedimentary particles gradually become fine from course, i.e. a gradual transition from the large-grained pebbles to the sandy, oviposite-gravel layer. The groundwater under flatlands is dominated by interstitial water in quaternary loose rock mass and its recharge comes from atmospheric precipitation infiltration, seepage of surface water and irrigation water, lateral inflow of mountainous area. [15] The formation lithology is mainly sandstone, quartzite, and quartz sandstone in the area, which could influence the deep groundwater quality. Nitrate nitrogen in groundwater under the fruiter planting area is easily influenced by precipitation, irrigation and fertilization because of its hydrogeological feature, although samples were collected from deep well depth. The maximum nitrate nitrogen (105.39 mg/L) was the test result of a sample collected from well located near the peach orchard with the depth of 320 m.

As we can see from Figure 5 and Table 4, in most cases the annual average concentrations of nitrate nitrogen in groundwater sampled from orchard were higher than which sampled from the other kind of agricultural field. Meanwhile, the average nitrate nitrogen in groundwater sampled from orchard often had larger variation than that from the other kind of agricultural field. It was indicated that there were some important influences on groundwater caused by fruiter planting. The annual average concentrations of nitrate nitrogen in groundwater tent to be gradually increased since the year of 2010 (Fig 1) especially for samples collected from orchard (Fig 5). An increase of GOVoAg, Output of PBL and Output of eggs over the period could be found [13]. The soil in Pinggu district is mostly sandy and permeable [17]. Research in Pinggu district showed that the nitrate in the groundwater mainly came from the nitrate produced by soil organic nitrogen mineralization. Sources of soil organic nitrogen include intermediates of organic decomposition, organic fertilizer applied, metabolites and secretions of microorganisms and roots, etc. Soil organic matter also include organic matter inherent in soil and organic fertilizer added externally [18]. According to Ren Huiqin’s study, organic fertilizer is an important nitrogen source of orchard and vegetable system in Pinggu [19]. Taking peach planting for example, 83% farmers use organic fertilizer as the basal fertilizer including pig manure, chicken manure and mixed manure which are easy to mineralize. It could be inferred that with the increase situation of output of PBL and output of eggs in Pinggu district more organic
fertilizer were getatable and applied to orchard. Besides the soil characteristics, large amounts of organic fertilizer application could be one of the important reason that made annual average concentrations of nitrate nitrogen in groundwater increase. Excess organic nitrogen remains in the soil, mineralized over time to produce nitrate, which threaten groundwater with rain or irrigation leaches into it [19]. It was shown that nitrate nitrogen in groundwater collected from vegetable field and grain field increased obviously since the year of 2013. There were some peak values of nitrate nitrogen in groundwater sampled from orchard and vegetable field from 2014 to 2017, which implied that the nitrate problems in groundwater of orchard and vegetable field should be paid more attention nowadays.

![Graph showing nitrate nitrogen concentrations in groundwater](image)

**Figure 5.** Mean values and C•Vs of groundwater nitrate nitrogen from different landuse types in different monitoring times.

**Table 4.** Statistical parameters of nitrate nitrogen in groundwater of different agricultural land use types in different monitoring times.

| Item                  | Orchard | Vegetable Field | Grain Field |
|-----------------------|---------|-----------------|-------------|
| C•V (%)               | 132.9   | 102.5           | 90.5        |
| Minimum (mg/L)        | 0.10    | 0.21            | 0.01        |
| Maximum (mg/L)        | 105.39  | 19.47           | 33.81       |

3.3. The nitrate nitrogen characteristic of different well depth

Groundwater samples were from 3 different types of wells according to the depth where it permeated. Types of wells are respectively spring well (WD1), well with the depth of 30 to 100 m (WD2) and well deeper than 100 m (WD3). The results showed that the average concentration of nitrate nitrogen in groundwater from WD1, WD2 and WD3 were 4.46 mg/L, 4.85 mg/L and 7.98 mg/L respectively (Fig 6). The variance analysis of nitrate nitrogen in groundwater sampled from these 3 well types showed that the nitrate nitrogen in groundwater from WD3 was significantly higher than which from WD1 and WD2, while there was no marked qualitative difference between the nitrate nitrogen in groundwater sampled from WD1 and WD2. 22.4% of the samples collected from well type of WD2 and 79.5% of the samples collected from well type of WD3 were around the orchard. The deeper well always located in mountainous area, where the fruiter planted and more fertilization opportunities occurs. The hydrogeological feature where deeper wells usually located plays an important role in
influencing the quality of deep groundwater [15]. It could be concluded that in Pinggu district the
deeper groundwater was permeated and collected from the well, the higher of the nitrate nitrogen
would be. The average well depth of the groundwater sampled from orchard was significantly higher
than well depths of the groundwater sampled from grain field and vegetable field (Fig 4), which could
be one of the explanations why the nitrate nitrogen in groundwater sampled from orchard was
markedly higher than which from grain field and vegetable field.

![Graph](image)

WD1: Spring well; WD2: Well with the depth of 30 to 100m; WD3: Well deeper than 100m

**Figure 6.** Mean values and C•Vs of groundwater nitrate nitrogen from different types of well in
different from 2006 to 2017.

4. Conclusion
The mean value of nitrate nitrogen of all samples collected from 2005 to 2017 in Pinggu district was
6.23 mg/L which made the water quality reach the third level of the national groundwater quality
standard. The nitrate nitrogen in groundwater of the monitored region had a rising trend in recent years.
It showed some significant positive correlations between the annual average concentrations of nitrate
nitrogen in groundwater and the statistical data of livestock and poultry products from 2006 to 2015.
There was a significant positive correlation (significant at the 0.05 level) between the C•Vs of nitrate
nitrogen calculated annually and the accumulated annual precipitation from 2006 to 2015. The
increase of precipitation has a trend of increasing the difference of nitrate in groundwater in Pinggu
district.

The nitrate nitrogen in groundwater sampled from orchard was markedly higher than which from
grain field and vegetable field. Samples from deeper well (WD3) always located in mountainous area,
the nitrate nitrogen in them was significantly higher than which from spring well (WD1) and well with
depth of 30 to 100 m (WD2).

Acknowledgments
This work was financially supported by the Project of construction of basic data platform for
agricultural scientific research in Special Project on Building of Scientific and Technological
Innovation Capacity of BAFFS (Project No. KJCX20160303), the Project of regional collaborative
innovation in Special Project on Building of Scientific and Technological Innovation Capacity of
BAFFS (Project No. KJ CX20180708) funds and the Ministry of Agriculture (Project No.
09182110402291004).

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