Geochemical characteristics and environmental quality assessment of fluorine in soil and water environment of Jinbei

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Abstract. Fluorine is a necessary trace element in humans, lack or excess can adversely affect human health. The geochemical characteristics and environmental quality of fluorine in soil and water environment of Jizhou district in northern Tianjin were studied. The results show: fluorine content in surface soil 201×10^{-6} ~8545×10^{-6}, average 757×10^{-6}. The average content is the background value of surface soil in Tianjin 1.25 times twice, all over the country 1.58 times twice. In soil vertical profiles, the content of fluorine in clay soil is higher than that in sandy soil. The average groundwater fluorine content in plain area 1.50 mg /L, average mountain area 0.47 mg /L. Plain area is obviously larger than mountainous area. Over the whole district 90% the fluorine content of surface soil showed excess and high level. Proportion of groundwater samples in plain area with fluoride class IV and class V water 61.54%. Fluorine excess ratio in maize samples 26.67%. Maximum excess multiple greater than 2 times twice. Overall, the fluorine content in the surface soil and the groundwater in the plain area of North Tianjin is significantly higher. For high-fluorine areas, the fluorine content of some bulk agricultural products has exceeded the standard. We should pay attention to it.

Key words. Jizhou District; fluoride; geochemical characteristics; environmental quality; ecological effects.

1. Introduction
Fluorine is a necessary trace element in humans, fluorine deficiency or overdose can adversely affect human health. Lack of fluoride affects bone development, causes dental caries and massive bone disease. Excessive fluoride in the soil can contaminate surface and groundwater, and then passed through the food chain to cause fluorosis. Soil is the hub of fluorine environmental chemistry system, fluorine has many occurrence forms in soil. Different forms of soil pH value, organic matter, clay, soil parent material and other factors.

Many parts of the country have been affected by fluorine to varying degrees. High fluorine groundwater distribution in North China Plain. Long-term use of high-fluorine groundwater for irrigation of farmland. That could lead to higher levels of fluoride in farmland. May cause excess fluoride in bulk food crops and vegetables. On the Surface Soil of Jizhou in northern Tianjin. Soil vertical profile, groundwater, geochemical characteristics of fluorine in surface water and crops. Environmental quality assessment and preliminary analysis of the causes. For the future regional related
research and government management provide scientific basis. It also provides important reference for the management of endemic fluorosis.

2. Survey Area
Tianjin is located in the northeast of north China. The study area is located in Jizhou District, the northernmost part of Tianjin. Lower and middle mountains in the north. Flood alluvial in the south — alluvial plain geomorphology. Large outcrop of bedrock strata in northern mountainous area. The buried depth of bedrock in the area covered by Quaternary system is also shallow. The bedrock strata are mainly middle, the Great Wall of the upper Proterozoic, JiXian and Qingbai Kou. The lithology is mainly carbonate rocks, shale, sandstone class. Magmatic activity is more intense in mountainous areas. PanShan granite of the indosinian period, stone mortar, Zhulyu Changyan. The intrusive rock mass of Beishan Chang porphyry. Among them, PanShan granite body has the largest scale. The groundwater in mountainous area is dominated by carbonate karst fissure water. The southern plain area is mainly covered by Quaternary strata, stable distribution, groundwater is mainly Quaternary pore water. Surface water is mainly the state river, channels.

3. Sample Collection and Analysis

3.1. Surface Soil Samples
Basis Multi-objective Geochemical Survey Specifications (DD 2005-01), Geochemical Assessment of Land Quality (DZ/T0295-2016), regional surface soil sample layout, collection and processing. The surface soil is distributed evenly by the method of gridding and plot combining. Position the center of the sampling point at the center of the plot. At the centre and near 20m scope 4 collection 0~20 cm deep soil combination 1 samples. Total acquisition 5782 sample soil samples, average sampling density in plain areas 7.0/km$^2$. Average sampling density in mountain orchards10/km$^2$. Average sampling density of forest land in mountainous areas 1/km$^2$. The original mass of each sample is greater than 1 kg. After natural drying in the room 10 Nylon sieve. Screening samples 200g paper bags for laboratory analysis of elemental content.

3.2. Soil Profile Sample
Soil profile samples were uniformly arranged in plain areas, the interval is 0~20 cm, 20~40 cm, 40~60 cm, 60~80 cm, 80~100 cm, 100~120 cm, 120~150. Sampling of each profile 7 Parts. Considering the thin soil cover in mountain areas. Many orchard soils are only thick 30~50 cm. No profile samples collected. The original mass of each sample is greater than 1 kg. After natural drying in the room 10 Nylon sieve. Screening samples 200 g paper bags for laboratory analysis of elemental content.

3.3. Groundwater and Surface Water Samples
Uniform collection of groundwater samples 47 parts. Sampling after pumping water for half an hour, washing sample bottles and stoppers before sampling 3~5 times. Interception at pump port. Surface water samples were collected mainly for farmland irrigation in the southern plain area. The largest river in the region state river. Uniform collection from ups tream to downstream 7 surface water samples. Gathered in a river in the southern part of the area a surface water samples. Collection of water samples from abundant ditches 3 parts. Surface water samples collected 11 parts. All samples collected 24h inside for laboratory testing.

3.4. Sample of Crops
Bulk agricultural wheat and maize seed samples collected in plain areas. Mountain area collection of special fruit products persimmon, chestnut, acid pear, apple, red fruit. Wheat and corn seed samples collected separately 30 parts. Collection of fruits and agricultural products 15 parts. Test methods and test basis for various samples are shown in Table 1.
Table 1. Matching Scheme of Fluorine Analysis Method for Various Sample

| Sample Type | Methodologies          | Test Methods      | Testing Basis       |
|-------------|------------------------|-------------------|---------------------|
| soil        | 0.5000g sample, alkali melting | Selective Ion Electrode Method | DD 2005-01          |
| groundwater | Selective Ion Electrode Method | DZ/T0064.54-1993  |                     |
| wheat, corn | proliferation          | F Reagent         | GB/T5009-2003, DD2005-03 |
| fruit       | proliferation          | F Reagent         | GB/T5009-2003, DD2005-03 |

4. Geochemical Characteristics of Fluorine in Different Media

4.1. Geochemical Characteristics of Surface Soil Fluorine

5782 results of fluorine content test and analysis in surface soil, minimum fluorine content in surface soil 201×10^-6, maximum value 8545×10^-6, median value 657×10^-6, standard deviation 141, average value 757×10^-6, coefficient of variation 18.63%. The average content of fluorine of surface soil in TianJin is 1.25 times. Therefore, the overall fluorine content in surface soil of this area is relatively high.

4.2. Geochemical Characteristics of Soil Fluorine in Profiles

To study the distribution of fluorine in soil at different depths. Layout in cultivated land in plain area with deep and uniform soil layer 7 soil profile. Collection cm 0~150 Soil samples at different depths within range. Fluorine in soil was tested. Previous studies have shown, distribution of fluorine in soil and soil clay content and pH value related. Soil viscosity heavy fluorine content is relatively high. Relatively low fluoride content in sandy soils. The trend of fluorine content in soil vertical profile is related to the distribution of clay layer. The increase of soil fluorine content with clay composition.

4.3. Characteristics of Fluorine Content in Groundwater and Surface Water

The groundwater aquifer in plain area is mainly composed of Quaternary loose strata. From Table 2, fluorine content ranges 0.32~4.89 mg/L. Average value1.50 mg/L, median value 1.13 mg/L, the highest value in East Shigu. The groundwater aquifer in mountainous area is mainly composed of bedrock strata such as granite or carbonate rock. Fluorine content ranges <0.20 (Below detection limit) ~ 2.55 mg/L, average value 0.47 mg/L, median value 0.32 mg/L, the highest value in Xujiatai. From the data distribution as a whole, the groundwater fluorine content in plain area is larger than that in mountainous area.

Surface water comes mainly from rivers or canals used for farmland irrigation in the southern plains. From Table 3, surface water fluorine content ranges 0.24 mg/L~1.00 mg/L, average value 0.59 mg/L, median value 0.60 mg/L. The overall fluorine content in the surface water used for farmland irrigation in the southern plain is low.
### Table 2. Distribution Characteristics and Environment Quality Assessment of Groundwater Fluoride in Plain and Mountain Areas of Jizhou

| Sample NO. | Geographical | Welldepth /m | Fluoride /(mg/L) | Sample NO. | Geographical | Welldepth /m | Fluoride /(mg/L) |
|------------|--------------|--------------|-----------------|------------|--------------|--------------|-----------------|
| JP1        | Mashenqiao   | 100          | 0.86            | JS1        | Xiaying      | 100          | 0.32            |
| JP2        | Chutouling   | 160          | 1               | JS2        | Xiaying      | 15           | <0.20           |
| JP3        | Chutouling   | 30           | 0.32            | JS3        | Xiaying      | 30           | 0.5             |
| JP4        | Xilonghuu    | 110          | 0.56            | JS4        | Luozhuangzi  | 208          | 0.5             |
| JP5        | Guili        | 70           | 0.92            | JS5        | Chuanfangyu  | 330          | 0.45            |
| JP6        | Guili        | 70           | 2.92            | JS6        | Sungezhuangzi| 30           | 0.96            |
| JP7        | Wubaihu      | 60           | 0.32            | JS7        | Sungezhuangzi| 15           | 0.25            |
| JP8        | Biesha       | 120          | 0.51            | JS8        | Guanzhuang   | 70           | 0.32            |
| JP9        | Youguzhuang  | 60           | 2.45            | JS9        | Luozhuangzi  | 200          | 0.29            |
| JP10       | Dongerying   | 60           | 3.1             | JS10       | Chuanfangyu  | 130          | 0.7             |
| JP11       | Dongzaoge    | 100          | 1.6             | JS11       | Xujiatai     | 44           | 0.27            |
| JP12       | Limingzhuang | 60           | 2.1             | JS12       | Guanzhuang   | 14           | <0.20           |
| JP13       | Bieshan      | 50           | 0.7             | JS13       | Guanzhuang   | 70           | 0.26            |
| JP14       | Yangjinzhuang| 60           | 1.68            | JS14       | Yuyang       | 130          | <0.20           |
| JP15       | Houjiaying   | 120          | 2.65            | JS15       | Baidong      | 100          | 0.25            |
| JP16       | Dongshi      | 70           | 4.89            | JS16       | Xujiatai     | 20           | 0.26            |
| JP17       | Yangjinzhuang| 100          | 2.49            | JS17       | Baidong      | 90           | 0.25            |
| JP18       | Yangjin      | 60           | 1.81            | JS18       | Xujiatai     | 100          | 2.55            |
| JP19       | Xiawotou     | 100          | 1.87            | JS19       | Baidong      | 70           | 0.42            |
| JP20       | Houjiaying   | 80           | 1.31            | JS20       | Bangjun      | 80           | 0.39            |
| JP21       | Yangjinzhuang| 100          | 1.13            | JS21       | Xiaying      | 30           | 0.55            |
| JP22       | Yangjinzhuang| 50           | 1.08            |           |              |              |                 |
| JP23       | Yangjinzhuang| 50           | 1.08            |           |              |              |                 |
| JP24       | Xiacang      | 70           | 0.79            |           |              |              |                 |
| JP25       | Xiacang      | 60           | 1.13            |           |              |              |                 |
| JP26       | Xiacang      | 90           | 0.7             |           |              |              |                 |

Min 0.32 Max 4.89 Average 1.5 Med 1.13

### Table 3. Distribution Characteristics and Environmental Quality Assessment of Surface Water Fluorine in Jizhou District

| Sample NO. | Geographical | Water  | Fluoride /(mg/L) |
|------------|--------------|--------|-----------------|
| JB1        | Yinliu       | Zhouhe | 0.24            |
| JB2        | Xiacang      | Zhouhe | 0.34            |
| JB3        | Shangcang    | Zhouhe | 0.35            |
| JB4        | Shangcang    | Zhouhe | 0.41            |
| JB5        | Yangjinzhuang| Zhouhe | 0.60            |
| JB6        | Xiacang      | Zhouhe | 0.65            |
| JB7        | Xiacang      | Zhouhe | 0.86            |
| JB8        | Sangzi       | Quhe   | 0.70            |
| JB9        | Houjiaying   | Qushui | 0.60            |
| JB10       | Xiawotou     | Qushui | 0.73            |
| JB11       | Xiacang      | Qushui | 1.00            |

Min 0.24 Max 1.00 Average 0.59 Med 0.60
5. Eco-environmental Effects of Fluorine
Crop cultivation in Jizhou district is relatively stable. Major crops, wheat and corn in plain areas. Mountain crops mainly chestnut, apple, red fruit, persimmon, all kinds of fruit trees such as pears. From Table 4, wheat, chestnut, apple, red fruit, persimmon, the content of fluoride in pear was lower than the standard limit. But corn 8 sample exceeding standard, excess ratio 26.67%, maximum excess multiple twice greater.

Table 4. Characteristics and Evaluation of Crop Fluorine Content in Jizhou District

| Crops      | Sample NO. | Range/10^-6 | Average/10^-6 | Standard/10^-6 | Overstandard |
|------------|------------|-------------|---------------|----------------|--------------|
| wheat      | 30         | 0.30~0.80   | 0.56          | 1.0            | 0            |
| corn       | 30         | 0.38~3.41   | 1.21          | 1.5            | 8            |
| chestnut   | 15         | 0.09~0.24   | 0.16          | 0.5            | 0            |
| apple      | 15         | 0.04~0.24   | 0.15          | 0.5            | 0            |
| red fruit  | 15         | 0.03~0.12   | 0.08          | 0.5            | 0            |
| persimmon  | 15         | 0.02~0.06   | 0.04          | 0.5            | 0            |
| pear       | 15         | 0.02~0.04   | 0.03          | 0.5            | 0            |

6. Conclusion
Soil in Jizhou District, northern Tianjin groundwater, geochemical characteristics of fluorine in crops, environmental quality assessment. The results show: Minimum fluoride content in surface soils $201 \times 10^{-6}$, maximum $8545 \times 10^{-6}$, average value $757 \times 10^{-6}$. The average fluoride content is the background value of the surface soil in Tianjin 1.25 times. All over the country 1.58 times. It shows that the overall fluorine content in the surface soil is relatively high. Fluorine content in soil vertical profile is related to soil texture. The content of fluorine in clay soil is higher than that in sandy soil. The range of groundwater fluorine content in plain area 0.32~4.89 mg /L, average value 1.50 mg /L. Overall, the groundwater fluorine content in plain area is larger than that in mountainous area.

The content of fluoride in wheat, chestnut, apple, red fruit, persimmon, pear was lower than the standard limit. But the fluorine excess ratio of corn samples excess multiple twice greater. It should be noticed by relevant departments.

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