Study on pollution characteristics of perfluorinated compounds in shallow groundwater system

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Abstract. In this paper, the pollution of perfluorinated compounds (PFCs) in the Groundwater system of a fluorine chemical industrial park is taken as the main research object. By selecting samples from shallow groundwater monitoring points, using factor analysis method and fuzzy clustering analysis method to study the pollution characteristics of shallow groundwater PFCs in this area, this study concludes that the concentration of PFCs in shallow groundwater in wet season is higher than that in dry season, only the change of pollution area is not obvious. At the same time, it is found that the variation of water level in the groundwater system is roughly positively correlated with the change of PFCs concentration.

1. Introduction

Perfluorinated compounds (PFCs) are synthetic chemicals used in fire-fighting foams, industrial surfactants, insecticides, and paper and textile surface treatments [1,2] . Because of their thermal and chemical stability, PFCs are environmentally persistent[3-5] . They are present globally in environmental matrices, including surface water, groundwater and sediment, even in remote locations[6].The sources of groundwater PFCs are mostly based on ground pollution sources, and enter the groundwater through the aeration zone. The distribution of groundwater PFCs under ground source pollution is affected by the adsorption capacity of the aerated zone soil [7,8].

The study area belongs to the piedmont slope alluvial plain area, the Dongzhulong River in the area (indicated by the DZL River in the test), the XizhuLong River (indicated by the XZL River in the test) and the Yuejin River(indicated by the YJ River in the test) have a greater impact on the industrial park area.The Quaternary loose rock layers in the study area are widely distributed. The shallow groundwater in the study area is mainly replenished by atmospheric precipitation replenishment and river channel leakage, followed by irrigation backflow recharge. The main excretion method is farmland irrigation and excretion, followed by evaporation and groundwater runoff excretion. The water level in the shallow groundwater level during the wet season is significantly higher than that in the dry season. The water level difference is up to 10.5m and the average water level varies by about 3m.

The purpose of this study is to study the pollution characteristics of typical pollution sources of shallow groundwater system PFCs, to identify the types of PFCs pollution sources, pollutant concentrations, pollutant distribution patterns and pollution characteristics of typical pollution sources in the study area.The mechanism of PFCs pollution in the shallow groundwater system of the study area was identified, which is of great significance for the monitoring, control, prevention and control of groundwater PFCs pollution.

2. Distribution of sampling points

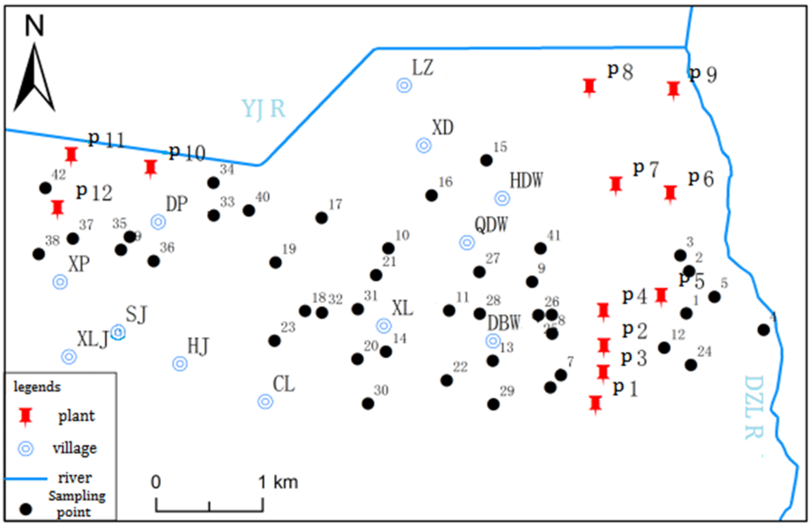

Figure 1. Distribution of groundwater sampling points

We conducted a reasonable layout of the sampling points. There were 42 water sampling points be selected, the sampling point distribution of specific locations shown in Figure 1. Sampling points are basically distributed downstream of the polluting enterprises.

3. Sample test result

According to the results of the water samples tested, the fluoride fluoride industrial park shallow groundwater monitoring indicators of the specific conditions shown in Table 1.

Table 1. PFCs different components of the detection rate and concentration of the list

Detection Indicator	Carbon chain length	Number of test points	The detection rate(%)	Minimum (μg/L)	Maximum (μg/L)
PFBS	4	42	7.14	nd	0.023
PFBA	4	42	92.80	nd	54.549
PFPeA	5	42	85.70	nd	22.389
PFHxA	6	42	90.60	nd	11.639
PFHxS	6	42	19.04	nd	0.240
PFHpA	7	42	61.90	nd	5.290
PFOA	8	42	100.00	0.005	343
PFOS	8	42	52.38	nd	0.234
PFNA	9	42	38.00	nd	0.112
PFDA	10	42	23.80	nd	0.099
PFDoDA	12	42	19.04	nd	0.162

As can be seen from Table 1, there are 11 PFCs detected in all the shallow groundwater samples collected, of which PFOA, PFBA, PFHxA) Had the highest detection rate of 100%, 92.8% and 90.6%. Analyze its reason, the industrial park to produce polytetrafluoroethylene and other fluoropolymer as the main product.

4. discussion

4.1. shallow groundwater flow field on the impact of PFCs
It can be clearly seen from the isograms of groundwater level in Fig. 6 and Fig. 7 that there is an obvious groundwater level dropping funnel in the study area located about 3.5km west of the fluorine chemical industrial park,shallow groundwater presents a tendency to converge from all directions to the landing funnel zone. It can be seen from the pollution distribution of PFCs that the pollutants of PFCs in shallow groundwater show the same pollution distribution as those of shallow groundwater flow.

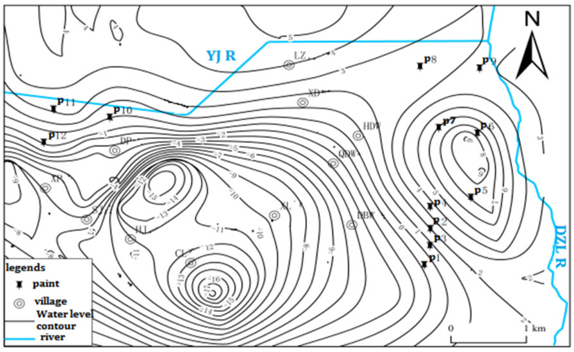

Figure 2. shallow groundwater level in dry season

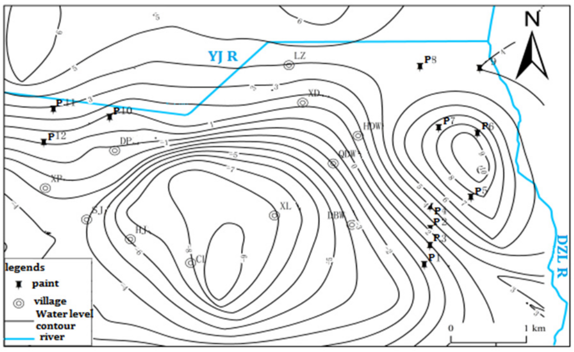

Figure 3. shallow groundwater level in wet season

Comparing Figure 2 and Figure 3, the center position of the shallow groundwater level drop funnel in the study area did not move significantly during the wet and dry season, indicating that the migration direction of PFCs in the study area did not change in shallow groundwater. However, the groundwater level changes more obviously， this is due to the influence of precipitation recharge and confluence. The groundwater level varies greatly in the center of the landing funnel, with an average of about 6m; other locations are smaller. In addition, the hydraulic gradient is also affected. From the fluorine material fluoride industrial park to the center of the groundwater drop funnel, the hydraulic gradient is about 5 ‰ in the wet season, but the hydraulic gradient is about 8 ‰ in the dry season, which causes a change in the groundwater flow rate. Compared with the dry season, the hydraulic gradient decreases and the flow rate slows down, which makes the PFCs pollution spread in the north-south direction relative to the dry season.

4.2. Shallow groundwater level changes on the impact of PFCs
PFCs enter the shallow groundwater system and exist in two forms, one is directly into the aquifer and dissolved in the groundwater; the other is the adsorption remaining in the vadose zone. The periodic variation of shallow groundwater in the study area is obvious. The lowest water level appears in May-June, and then enters the wet season.， the precipitation increases, the recharge volume becomes larger, and the water level begins to rise. The water level reaches its peak in September-October. We selected a water level monitoring point at the center of the shallow groundwater level drop funnel in the study area and a water level monitoring point in the non-funnel center area. The monthly average water level values of the two water level monitoring points in 2017 are shown in Figure 4 and Figure 5. It can be seen from Figure 4 and Figure 5 that the shallow groundwater level in the region is in a downward trend from January to May, and gradually increases from June to September. After September, the precipitation gradually decreases, the recharge decreases, and the shallow layer The groundwater level began to fall.

It can be seen from the figures that the shallow groundwater in the center of the funnel has a large change in water level during the wet and dry season, and the water level is low; the shallow groundwater in the non-funnel center area has a smaller variation in the wet and dry season, and the water level is relatively high.

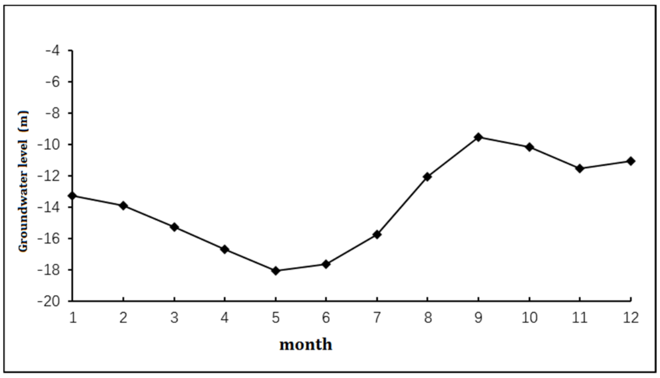

Figure 4. Monthly average of shallow groundwater table in the funnel center of 2017

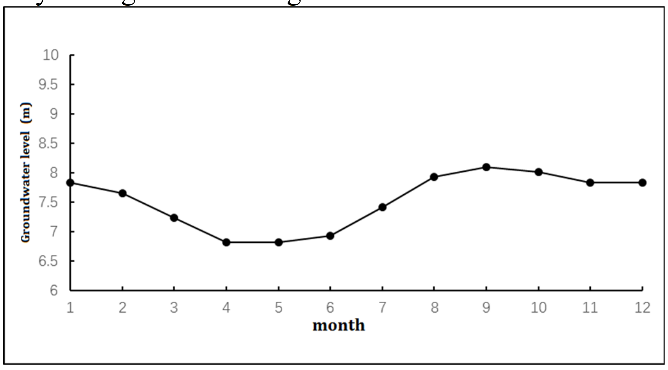

Figure 5. Monthly average of shallow groundwater table in non-funneling center of 2017

Changes in shallow groundwater levels in the study area caused changes in PFCs. The concentration of PFCs in the shallow groundwater during the wet season was significantly higher than that in the dry season. Taking the No.1 monitoring well and the No.25 monitoring well as examples, the PFCs concentration in the dry season was 363.69μg/L and 411.44μg/L, respectively. The concentration in the wet season was 723.86μg/L and 822.82μg/L, respectively, and the average increase was about 2 times. Taking the monitoring wells No. 18, 32, and 20 located near the groundwater level falling funnel area as an example, we found that the concentration of PFCs in the dry season is 0.08 μg/L, 0.06 μg/L, and 0.09 μg/L, respectively. The concentration in the wet season was 0.37μg/L, 0.25μg/L, and 0.32μg/L, respectively. The concentration in the wet season was about 4 times that in the dry season. It can be concluded that the concentration of PFCs in shallow groundwater with large changes in water level varies greatly, which is related to the adsorption of soil in the aeration zone and precipitation. In addition, the aquifer in the study area is a porous medium environment. When PFCs migrate and diffuse in shallow groundwater, they are easily adsorbed to the aquifer medium, which results in a large difference in the concentration of PFCs in the shallow groundwater of the pollution source area and the downstream area of the groundwater.

The effects of shallow groundwater level changes on the distribution of PFCs in shallow groundwater systems in the study area are:

(1) During the wet season, the precipitation is high. Through leaching, the PFCs adsorbed in the soil of the aeration zone enter the shallow groundwater with the precipitation infiltration, resulting in an increase in the content of PFCs in the shallow groundwater;

(2) The shallow groundwater level rises, and the aerated zone with a certain thickness becomes a saturated zone under the elevation of the groundwater level. The PFCs adsorbed in the vadose zone enter

the shallow groundwater under analytical and dissolved conditions, causing an increase in the content of PFCs in shallow groundwater, which will increase the pollution area in the wet season. In the dry season, the amount of precipitation is small, the recharge is small, the artificial mining is serious, the groundwater level is reduced, and the pollution area is reduced.

In addition, the reason for the wide range of pollution is that in the process of producing PFOA and fluoropolymer, about 23% of the PFOA discharged into the environment will enter the air, adsorbed to the atmospheric particulate matter, and fall with the settlement. At a distant surface, under the leaching of precipitation, it enters the shallow groundwater system, resulting in a change in the content of PFOA in shallow groundwater.

5. Conclusions

1. There are 11 species of groundwater PFCs detected in the study area, of which PFOA is the most important pollutant. The shallow groundwater in the study area is generally polluted by PFCs, and the change of pollution area in the wet season and the dry season is less obvious. Concentrations of PFCs in shallow groundwater in wet season are higher than those in dry season.

2. Affected by the shallow groundwater flow field, PFCs migrate westward, resulting in a longer pollution distance. The variation of groundwater level causes the change of the concentration of PFCs in groundwater in time and space. The variation of water level is different, and the concentration of PFCs varies. The two basically show a positive correlation, which is related to the adsorption of aeration zone and aquifer medium.

Acknowledgment

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References

[1] Paul, A.G. ， Jones, K.C. ， Sweetman，A.J. (2009)A first global production, emission, and environmental inventory for perfluorooctane sulfonate.Environ. Sci. Technol., 43, pp. 386-392

[2] Prevedouros, K. ， Cousins, I.T. ， Buck, R.C. ， Korzeniowski，(2006)S.H. Sources, fate and transport of perfluorocarboxylates.Environ. Sci. Technol., 40 , pp. 32-44

[3] Hekster,F.M., Laane, R.W.P.M. , de Voogt,P. (2003)Environmental and toxicity effects of perfluoroalkylated substances.Rev. Environ. Contam. Toxicol., 179 , pp. 99-112

[4] Parsons,J.R., Saez, M.,Dolfing, J., Voogt,P de. (2008) Biodegradation of perfluorinated. compounds.Rev. Environ. Contam. Toxicol., 196 , pp. 53-71

[5] Sinclair, E., Kannan,K. (2006) Mass loading and fate of perfluoroalkyl surfactants in wastewater treatment plants.Environ. Sci. Technol., 40 , pp. 1408-1414

[6] Murakami,M., Koroda,K., Sato, N.,Fukushi, T., Takizawa,S.(2009) H.Takada Groundwater pollution by perfluorinated surfactants in Tokyo.Environ. Sci. Technol., 43 , pp. 3480-3486

[7] Becker, A.M.,Gerstmann,S., Frank,H.(2008) Perfluorooctane surfactants in waste waters, the major source of river pollution. Chemosphere, 72 , pp. 115-121

[8] Young,C.J., Furdui,V.I., Franklin,J., Koerner, R.M., Muir, D.C.G., Mabury,S.A.(2007)Perfluori nated acids in Arctic snow: new evidence for atmospheric formation Environ. Sci.Technol., 41, pp. 3455-3461