

Distribution characteristics of perfluorooctanoic acid (PFOA) in shallow groundwater of a Fluorine Industrial Park in Shandong Province

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Abstract. In this study, shallow groundwater level, the distributions of PFOA, and differences in wet and dry seasons were examined with a 3km radius from a mega-fluorochemical industrial park(FIP). Perfluoroalkyl acids (PFAAs) were found in all the samples, and perfluorooctanoic acid(PFOA) dominated. PFOA-containing waste discharged from the FIP was discharged into surface water then to shallow groundwater through seepage. Under the action of shallow groundwater flow, PFOA diffused along the direction of shallow groundwater flow, and with the increase of distance, the level of PFOA in groundwater showed a downward trend. In general, pollution range in the wet season is larger than that in the dry season, but this place is not the case. A huge underground funnel in the area played a role in intercepting pollution and controlling the scope of pollution, so the scope of pollution was not expanded. The changes of PFOA in the rainy and dry periods were analysed, and the content of PFOA in shallow groundwater, in the study area, was significantly higher than that in the dry season. For example, the concentrations of perfluorooctanoic acid (PFOA) of sample J1 in the low water period was 343µg/L, while in the wet season was 560µg/L.

1. Introduction

The manufacture of fluorochemicals can lead to high levels of perfluoroalkyl acids (PFAAs) Perfluoroalkyl acids (PFAAs) have some unique properties, including surface activity, repellence of water and oil, and resistance of acid and heat[1-2]. So, they are widely used in manufacturing processes and products, such as textiles, carpets, paint, video materials, aviation hydraulic oil surfactants and surface protectors, and performance chemicals. Due to the environmental persistence, toxicity, and bioaccumulation properties of PFAAs, concerns have been raised, so the production of PFAA-related chemicals has been discontinued in Europe and America, but it continues to increase in China due to the domestic and international demands.

In this study area, the major source is a Fluorochemical Industrial Park, a fluoropolymer production centres[3-4]. It was estimated that about 80–90% of PFOA/PFOS contamination was estimated to come directly from manufacturing and industrial sites mostly via wastewater discharge from these facilities[5]. Sewage discharged into the surface water system, with surface runoff, infiltration[4], leakage and other functions, ultimately, reached the groundwater system. In the west of the fluorine chemical plant is a large living area and large tracts of farmland and vegetable land, and the area of irrigation water mainly from shallow groundwater. Severe shallow groundwater pollution can contaminate irrigated surface soils, contaminants accumulate into crops and vegetables and ultimately have an impact on human



health[6-7]. Besides, high concentrations of PFAAs shallow groundwater could pose not only a potential health risk of drinking water but also a risk to wildlife in aquatic ecosystems [8-9]. It is tough to remove PFAAs by conventional drinking-water treatment processes [10]. Hence, it is very important to identify and control PFAAs contamination.

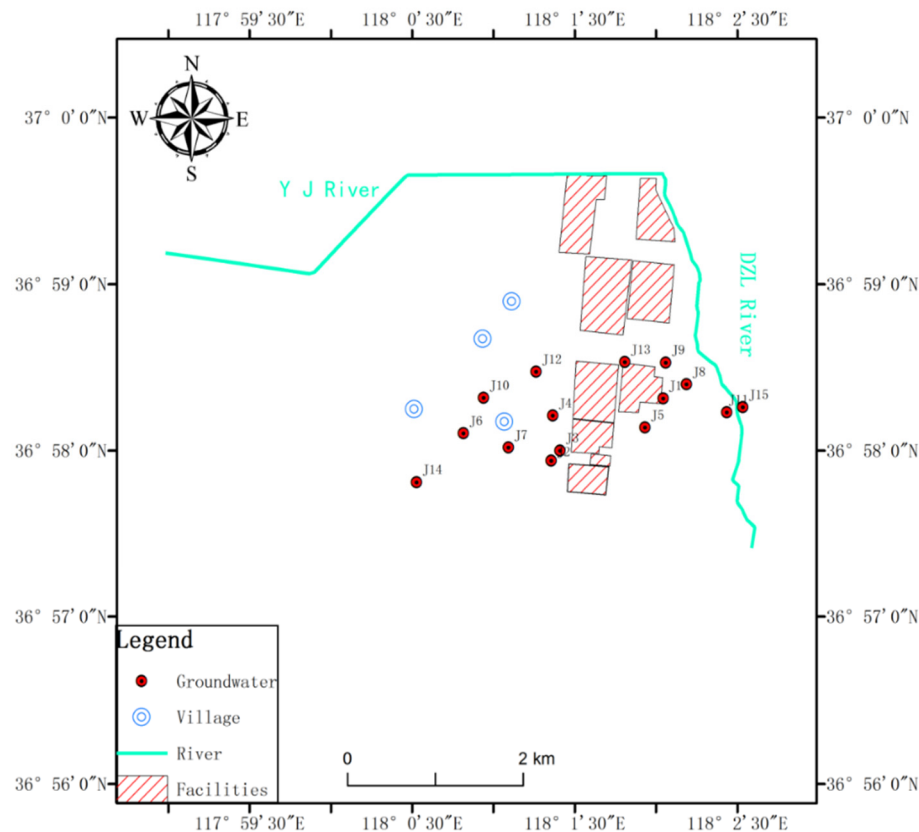


Figure 1. The distribution of groundwater sampling points.

2. Materials and methods

2.1. Data collections

Well water, as a typical shallow groundwater, because it is exposed directly to the outside, there is no pipeline protection, easy to be contaminated.

In order to examine the effect of the FIP on the surrounding shallow groundwater, the groundwater level was measured and the water samples were collected. In March 2016, 60 wells in the area were measured and 15 groundwater samples were collected. After the water sample is taken, it is kept in the bottle and is quickly sealed and frozen. The measured samples were sent to the Provincial Inspection Office for testing within one week. In August 2016, the same wells were measured and water samples were harvested.

Of 24 samples of the two periods, 12 PFAAs: perfluorooctanoic acid (PFOA), perfluorobutanoic acid (PFBA), perfluorohexanoic acid (PFHxA), perfluoropentanoic acid (PFPeA), perfluoroheptanoic acid (PFHpA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), perfluorododecanoic acid (PFDoA), PFOS and perfluoroundecanoic acid (PFUnDA), were detected.

2.2. Groundwater level simulation

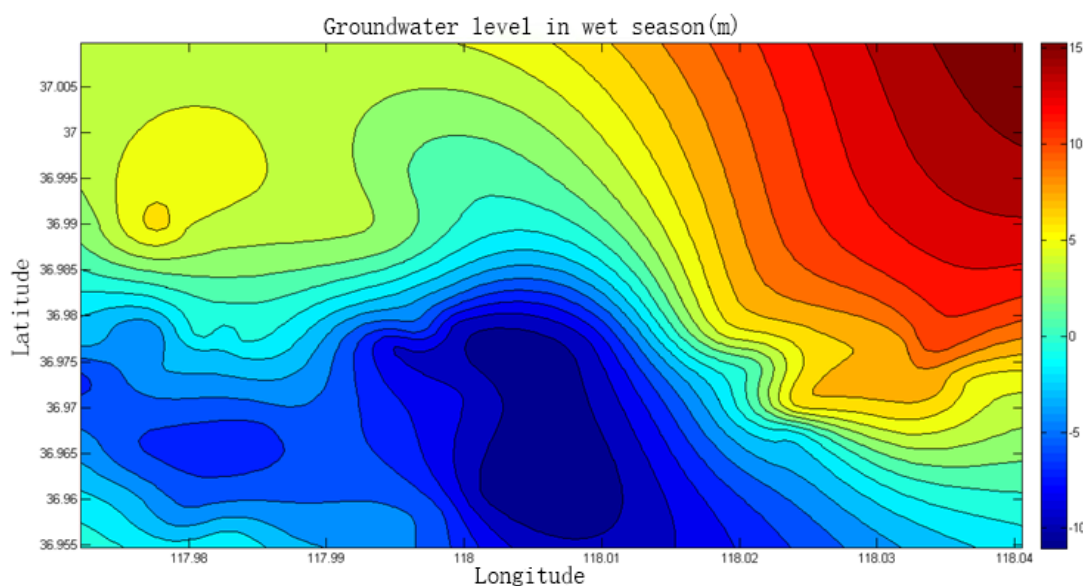


Figure 2. The contour map of the shallow groundwater levels

Groundwater flow affects the direction of migration of pollutants, so it is very important to analyze the trend of groundwater flow. After shallow investigation, the shallow groundwater level in the study area is slightly lower than that of the DZL River. The shallow groundwater is leached by the river. During the recharge process, river water together with contaminants leaked into the shallow groundwater system. The simulated groundwater level is simulated by MATLAB software. From figure2, Shallow groundwater flows from east to west, and finally comes into the funnel area

2.3. PFAAs analysis

Each of the 12 PFAAs was detected in this study. The concentrations of sum of PFOA dominated, with about 80% contribution to $\sum$ PFAAs in shallow groundwater. Therefore, perfluorooctanoic acid (PFOA) can be analysed as its characteristic contaminants when analysing the distribution characteristics of PFAAs and their pollution characteristics in shallow groundwater.

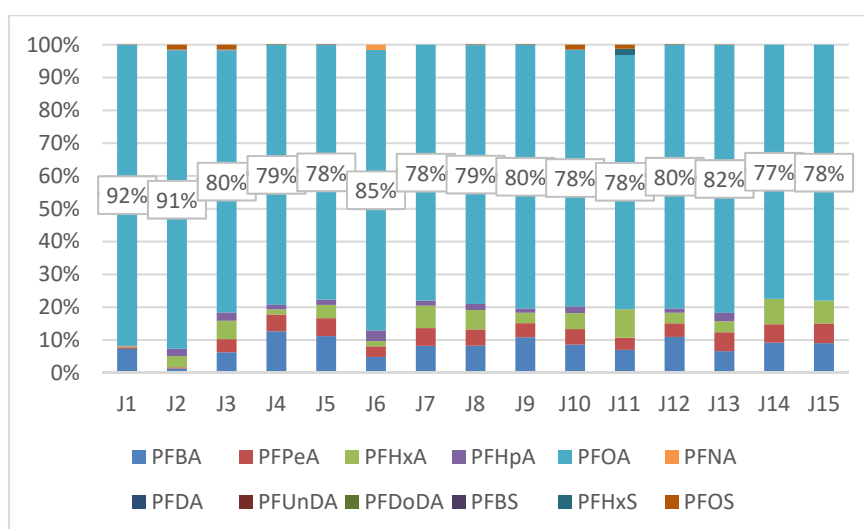


Figure 3. The relative abundance of PFOA.

3. Results and discussion

Analysis from the perspective of time, the data of PFOA concentration in shallow groundwater were divided into the dry season and wet season, simulation drew out the distribution map of PFOA compounds using the MATLAB software, in order to reveal PFOA distribution characteristics. Based on the measured two-phase concentration data, the PFOA concentration profile is plotted as follows.

Table 1. Concentrations of PFOA($\mu\text{g/L}$) in different seasons.

	Set	J1	J2	J3	J4	J5	J6	J7	J8
March	PFOA($\mu\text{g/L}$)	343	2.056	6.385	288.5	29.8	0.053	0.1145	89.5
August	PFOA($\mu\text{g/L}$)	560	5.202	8.355	298.59	30.7	0.055	0.1224	89.58
	Set	J9	J10	J11	J12	J13	J14	J15	
March	PFOA($\mu\text{g/L}$)	39.232	0.102	0.122	38.812	613	0.014	0.0078	
August	PFOA($\mu\text{g/L}$)	40.875	0.153	0.053	209.88	660	0.011	0.002	

3.1. Distribution of PFOA concentration in dry season

In dry season, perfluorooctanoic acid (PFOA) at J13 is the highest, reached 613 $\mu\text{g/L}$, position J13 wells located near the fluorine Industrial Park. PFOA at J4, with a concentration of 288.5 $\mu\text{g/L}$. Moving west from the FIP, the concentration of PFOA in groundwater sharply decreased by 99.9% (from 288.5 $\mu\text{g/L}$ to 0.1145 $\mu\text{g/L}$) within a distance of 500m. Once the distance had increased to 3 km from the FIP, the concentration of PFOA at J14 was 0.014 $\mu\text{g/L}$.

The FIP located in the eastern part of the study area is close to the eastern DZL River. The shallow groundwater is supplied by the river, under the action of the flow, perfluorooctanoic acid (PFOA) along the shallow groundwater flow direction diffusion fastest. Studies have shown that the eastern part of the river plays a very good role in isolation[4]. The concentrations of PFOA at site J11(0.1223 $\mu\text{g/L}$) was much higher than site J15(0.0078 $\mu\text{g/L}$) on the east side of the DZL river, which proved that the river has a blocking effect.

3.2. Distribution of PFOA concentration in wet season

From Figure 4, the distribution of PFOA in the wet season is similar to that of the rainless period. The PFOA concentration at J1(343 $\mu\text{g/L}$), J12(38.812 $\mu\text{g/L}$), J2(2.056 $\mu\text{g/L}$) in low water period was 309 $\mu\text{g/L}$, while in wet season was 560 $\mu\text{g/L}$, 209.88 $\mu\text{g/L}$, 5.202 $\mu\text{g/L}$. Obviously, the PFOA concentration is greater than the dry season. In general, the concentration of PFOA in dry season is higher than high water period. On the contrary, in the study area, the content of perfluorooctanoic acid in shallow groundwater is much higher than that in dry season. The Influence on the distribution of PFOA in the shallow groundwater system in the study area is as follows:

(1) During the period of abundant water, the precipitation increases, and the flue gas containing the PFOA discharged from the factory is descended to the surface and then into the shallow groundwater under the action of precipitation.

(2) The PFOA adsorbed in the unsaturated zone are introduced into the shallow groundwater under the influence of leaking water, resulting in the increase of the content of PFOA in the shallow groundwater.

(3) Where groundwater had become contaminated, surface water seepage was estimated to contribute about 50% of PFOS and 40% of PFOA while the remainder was mostly derived from soil leaching[5]. With the increase of the groundwater level, some of the unsaturated zone became saturated water, and the PFOA attached to the unsaturated zone was dissolved in the shallow groundwater under soaking, which increased the PFOA content in the shallow groundwater.

However, the total contaminated area was not changed compared with rainless period. From Figure 2, there is a huge underground funnel in the area, which plays a role in intercepting pollution and controlling the scope of pollution.

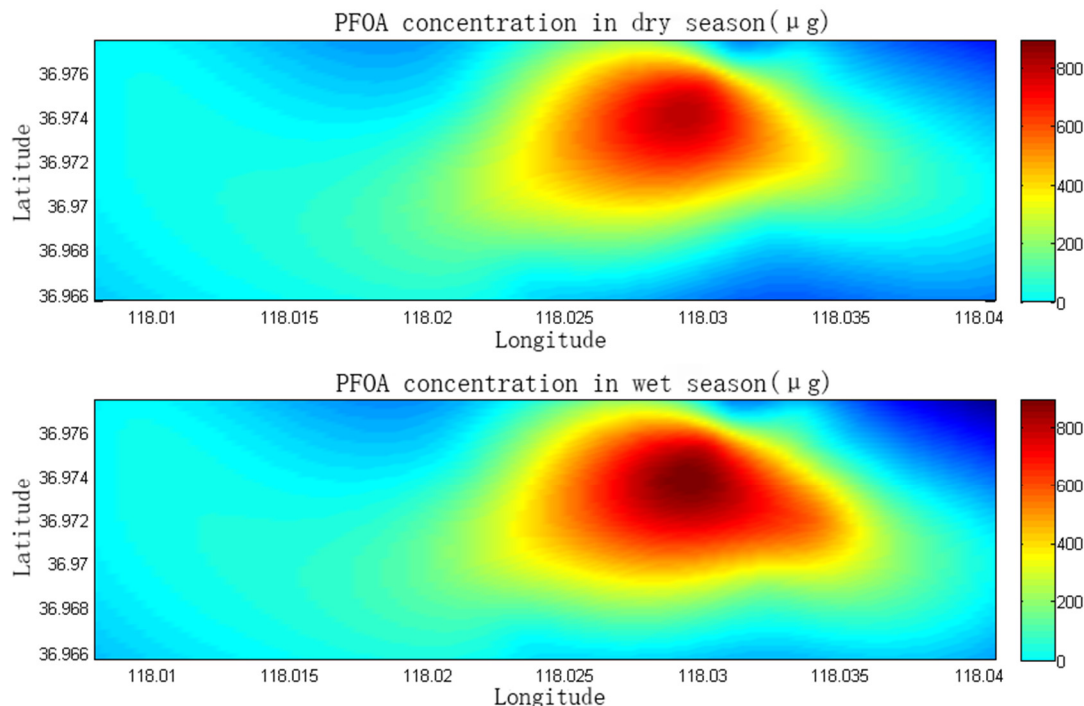


Figure 4. The concentration of PFOA in dry and wet seasons.

4. Conclusion

In this paper, shallow groundwater level, the distributions of PFOA, and differences in wet and dry seasons was analyzed. The pollution situation of PFOA is serious, and it spreads from the pollution center to the surrounding area. As the distance increases, the concentration of PFOA decreases gradually, and decreases gradually from east to west. The downward trend and the downward tendency of groundwater flow have higher similarity. Along the direction of the flow, perfluorooctanoic acid (PFOA) diffusion rate of the fastest, contaminated feathers appear narrow and long distribution. PFOA was the predominant PFAA with average relative abundance of 80.1%. The PFOA concentration in the wet season and the dry season was significantly greater than that in the dry season. Due to a huge underground funnel, the polluted area in March and August was similar.

Last but not least, it is of critical importance to ensure the safety of drinking water. To reduce PFOS/PFOA contamination of the Chinese environment the focus for control should be on industrial wastewater emissions. The relevant laws should be implemented as soon as possible, not just talk about it!

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