Per- and polyfluoroalkyl Substances (PFAS) In China’s Groundwater Resources: Concentration, Composition, and Human Health Risk

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Abstract. As an important class of emerging contaminants, per- and polyfluoroalkyl substances (PFAS) in water resources has been extensively studied. In this study, PFAS contamination in Chinese groundwater was systematically analyzed according to the reported literature. The research on PFAS in groundwater was concentrated in the eastern regions of China and that the concentrations of PFAS in groundwater ranged from N.D. to 26700 ng/L. The detected PFAS were PFBS, PFOA, PFBA, PFHxA, PFHxS, PFHpA, PFOS, PFPeA, PFUnA, PFTeDA, and PFNA. Among them, PFOA, PFBA, and PFBS showed higher concentrations. The concentration and composition of PFAS in groundwater varied significantly across different regions, often attributable to local industrial activities and urbanization. PFOA was the most commonly detected PFAS in the samples and also the primary contaminant in 14 sites. Additionally, PFPeA, PFBA, PFOS, and PFHxA also occupied a significant proportion of the total concentration level. The human health risk of various PFAS was assessed by the value of the predicted no effect concentration (PNEChum). The PNEChum value for PFOS, PFOA, and PFNA is relatively low, indicating a high risk to human health. Combined with the actual detection concentration, PFOS and PFOA are the two highest risk pollutants, which need attention and control. For the last decade, the concentration of PFOS has decreased, but the situation of PFOA was not encouraging. This study reviewed the PFAS contamination in groundwater in China, identified the high-risk substances, confirmed the need for regulation and control, and highlighted the importance of protecting public health during economic development.

1 Introduction

For several decades, Per- and polyfluoroalkyl substances (PFAS) have been widely used in various industries and everyday products, including metal plating, electronic etching baths, firefighting foams, food packaging, and textile coatings [1] [2]. PFAS are environmentally persistent and can transfer from water to soil or air, and even enter the food chain [3]. Consequently, PFAS have been detected in the blood of animals, such as giant pandas [4]. PFAS also poses a risk to human, for example, serum PFOA and PFOS are significantly associated with hypertension in adults [4][5]. Due to frequent detection and high toxicity, two long-chain perfluoroalkyl substances, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), have received great attention. Therefore, they were included in Annex B of the Stockholm Convention in 2009, restricting their production and use worldwide [6].

As a result of these limitations, a variety of alternatives have been introduced, including short-chain PFAS (C4-C6) and novel fluorinated substitutes [3]. Additionally, numerous polymorphs have been developed and widely utilized, such as 6:2 fluorotelomer sulfonate (6:2 FTS, CAS No. 27619-97-2) and potassium 9-chlorohexadecafluoro-3-oxanonane-1-sulfonate (F-53B, CAS No. 73606-19-6) [2]. However, recent studies have shown that these alternatives are also toxic and pose a risk to human health [7]. Furthermore, various PFAS substances, including short-chain PFAS and fluorine-modulated polymers, have been found in surface water, groundwater, coastal water, drinking water, and soil [8]. The highest concentration of PFAS, at 74.56 ng/L, was discovered in surface water of the Yangtze River, according to Pan et al. [9], Qiao et al. [10] discovered that the total concentration of 10 PFAS (Σ PFAS) in groundwater in northeast China ranged from 0.05 to 198.80 ng/L.

Previous studies have detected PFAS in various areas, including groundwater, which is a vital source of drinking water for a large population worldwide. In China, where almost 70% of the population and 40% of agricultural irrigation rely on groundwater, the contamination of PFAS in groundwater poses a significant health risk to residents, particularly in untreated rural areas [11]. Meanwhile, Groundwater is very stable and takes decades or even centuries to renew, once contaminated, remediation is very difficult. Besides,
China is also the leading producer and consumer of PFAS globally, with large amounts of PFAS entering the water recycling system annually \[12\] \[13\]. Therefore, investigating PFAS contamination in groundwater is crucial to assess potential health risks. However, research on PFAS in groundwater is limited compared to other water bodies, and an overview and analysis of PFAS concentration and composition in groundwater from various regions are still lacking.

The aim of this study is to evaluate the presence of PFAS in groundwater across different regions of China based on previous reports. The specific objectives include: (i) assessing and analyzing the concentration levels of PFAS in different regions; (ii) identifying the main constituents of PFAS in different regions; (iii) understanding the temporal and spatial variations of PFAS concentration; (iv) estimating the potential health risks of PFAS to local residents via groundwater. This work analyzed the current levels, composition, spatial-temporal characteristics, and human health risk of PFAS in groundwater in China, provided valuable guidance for mitigating the potential hazards of PFAS, and confirmed the necessity of supervision and control of high-risk PFAS.

2 Methodology

2.1. Data collection

Keywords such as PFAS, PFOA, PFOS, groundwater and China were used to search for publications related to PFAS levels in groundwater in China for the past fifteen years. A total of 17 studies on PFAS contamination in groundwater in various regions of China were found, including eastern, western, northeastern, and southeastern regions. Additionally, 25 studies related to PFAS contamination in other countries, including the United States, India, and Korea, were also identified.

2.2 Data Evaluation

To ensure the reliability of the data, we conducted a screening of the types of PFAS used for subsequent analysis. PFOS, PFOA, PFNA, PFBA, PFPeA, PFHxA, PFBS, PFHpA, PFHxS in groundwater samples from China were analyzed based on the results of uncertainty analysis (Supporting Information, S1). The extracted information such as study site, detection time, instrumentation, and total PFAS levels were listed in Table S2. The site-specific concentration data for each sampling point were organized in Table S3. According to the data quality assessment set by the US EPA, PFAS values that are considered non-detects based on the limit of quantification (LOQ) were substituted with a value of 0. The referenced articles mainly used liquid chromatography-mass spectrometry technique for PFAS analysis. Since most studies did not show complete data for each sampling site, the highest PFAS concentration detected in each study was used for statistical analysis in this study.

2.3 Human health risk

The potential impact of PFAS on human health is evaluated using the Predicted No Effect Concentration model (PNEChum). Assuming that adults primarily ingest contaminants in groundwater through drinking water, the calculation equation is:

\[
PNEChum = \frac{1000 \times \text{MRL} \times \text{BW} \times \text{AT}}{(\text{IngRDW}) \times \text{EF} \times \text{ED}}
\]

where the unit of PNEChum is ng L\(^{-1}\); 1000 is the conversion factor (conversion between µg/L and ng/L); the unit of maximum residue limit (MRL) is µg kg\(^{-1}\)·day\(^{-1}\); BW is body weight, the average weight of adults in China is about 61.5 kg; AT represents the averaging period and is fixed at 10950 days; IngRDW refers to the amount of drinking water consumed by an adult, set at 2 L·person\(^{-1}\)·day\(^{-1}\); EF is the exposure frequency, set at 350 d·yr\(^{-1}\); ED is the exposure time, set at 30 years. The MRLs for perfluorinated compounds were obtained from the US ATSDR [30]. In the absence of toxicity data, the MRLs were estimated using the threshold of toxicological concern (TTC), which is a conservative threshold for general human exposure to chemicals. If human exposure is below this threshold, the contaminant is not considered to pose a significant risk to human health. The Cramer categories, which are classified into three hazard classes (Cramer I, II, and III), were obtained from the ToxTree-v3.1.0.185 software.

3. Results and discussion

3.1 PFAS concentration levels in groundwater

Most of the articles cited in this paper were published in the last five years. A total of 39 sampling points were collected (see figure 1), mainly concentrated in East and North China, with Jiangsu Province having the most sampling points, 17 in total. There is only one sampling point in the western region, namely the Loess Plateau. Beijing, Tianjin, Jiangsu, and Jiangxi have more sample points, while data in the western region is very limited. This situation is related to the local economic development level and people's awareness of the hazards of PFAS in water.

Figure 1. Sampling locations
In Figure 2(a), the range of PFOS is N.D.-403 ng/L, with a median of 2.8 ng/L. The range of PFOA is 0.2-4150 ng/L, with a median of 8.15 ng/L. PFNA has a range of N.D.-8.13 ng/L, with a median of 2.035 ng/L. PFBA has a range of N.D.-21200 ng/L, with a median of 6.775 ng/L. PFPeA has a range of N.D.-290 ng/L, with a median of 14.29 ng/L. PFHxA has a range of N.D.-1180 ng/L, with a median of 4.01 ng/L. PFBS has a range of N.D.-21200 ng/L, with a median of 14.2 ng/L. PFHpA has a range of N.D.-766 ng/L, with a median of 6.775 ng/L. PFHxS has a range of N.D.-1140 ng/L, with a median of 0.985 ng/L. PFUnDA has a range of N.D.-11.82 ng/L, with a median of 1.925 ng/L. PFTeDA has a range of N.D.-9.21 ng/L, with a median of 0.64 ng/L. In order of median: PFPeA > PFBS > PFOA > PFBA > PFHxA > PFHpA > PFOS > PFNA > PFUnA > PFHxS > PFTeDA. However, in order of maximum concentration: PFBS > PFOA > PFBA > PFHxA > PFHpA > PFPeA > PFOS > PFPA > PFUnA > PFTeDA > PFNA. Overall, PFOA, PFBA, and PFBS have higher concentrations. Possible sources for the occurrence of PFAS in groundwater include: surrounding industrial activities, domestic sewage, solid waste, and soil pollution (firefighting, irrigation). Contaminated water is discharged into rivers and then enters the groundwater through the water cycle. PFAS in solid waste can also infiltrate the aquifer through soil. Pollutants released into groundwater are likely to accumulate and migrate with groundwater flow [14]. Hence, it is imperative that we pay attention not only to direct industrial pollution, but also to groundwater migration and soil leakage, as this indicates soil contamination as well [15].

As shown in Figure 2(b), there is a large variation in PFAS concentrations in groundwater across different regions, which is usually related to local industrial activities and urban development. Interestingly, some sampling sites located in Tianjin (TJ-03), Shandong (SD-01), and Jiangsu (JS-16) has very low PFAS concentrations, whereas the seemingly underdeveloped Loess Plateau (SX-01) has a high concentration of PFAS. This is because the low concentration samples were taken from drinking water sources or rural areas, while the sites on the Loess Plateau are located in China's largest new energy and chemical industry base. Extremely high levels of PFAS have been found in Liaoning (LN-01 and LN-02), with samples taken from household gardens near local fluoride-containing compound production facilities. Due to the high level of PFAS-related industrial activity and the lack of appropriate treatment of PFAS in wastewater, the pollution situation there is highly concerning.

3.2 Compositional profiles of PFAS in the groundwater

Figure 3 shows that there is a significant variation in PFAS composition among different regions. Out of the 39 sampling points, PFOA was the most prevalent PFAS component at 14 points, making it the most crucial PFAS composition. As PFOA is the most commonly detected PFAS, it is expected to be detected more frequently in environmental media [16]. PFOA poses significant environmental risks due to its detection frequency, toxicity, stability, and long-distance migration potential [3]. Moreover, PFBS was the most abundant component at eight sampling points, while PFPeA, PFBA, PFOS, and PFHxA dominated at six, six, three, and two sampling points, respectively. There were also five PFAS (PFNA, PFHpA, PFHxS, PFUnDA, and PFTeDA) that did not dominate any sampling point, indicating limited use. Although PFOS and PFOA were once widely used, due to their gradual production and use restrictions, short-chain alternatives such as PFBS, PFBA, PFHxA, and PFPeA are becoming mainstream. Short-chain PFAS mainly used in China include PFBA and PFBS. PFBS is commonly used as a catalyst in polymer manufacturing and chemical synthesis, as well as a stain repellent in leather, textiles, and carpets [17]. PFBA is commonly used in the biopharmaceutical industry, such as sequencing, synthesis, and dissolution of proteins and peptides [18].
PFOA was found to be the most abundant PFAS component in five provinces (Beijing, Fujian, Hebei, Shaanxi, and Tianjin). PFBA and PFPeA dominated in Jiangxi’s sampling points. There was an extremely high PFBS content in Liaoning. The situation in Jiangsu was the most complex, with several PFAS dominating, including PFOA, PFBS, PFPeA, PFOS, PFBA, and PFHxA. It is noteworthy that Jiangsu is a significant textile industry base in China, contributing around 20% to the country’s textile industry [29]. The complex composition also reflects the ongoing process of short-chain PFAS gradually replacing long-chain PFAS in China’s related industries. In Figure 3, the proportion of traditional PFOS and PFOA in some areas of Jiangsu’s groundwater samples is relatively low, suggesting that new perfluoroalkyl compounds are being used as substitutes in most of these areas in recent years, which is a positive development.

Figure 3. Composition of PFAS in groundwater in different regions

3.3 Human health risk of PFAS in groundwater

The PNEChum values are shown in Table 1. The range of PNEChum values is significant because the range of MRLs is large. As indicated by the formula in Chapter 2.3, MRLs have a decisive impact on the value of PNEChum. The order of PNEChum values from low to high is PFOS, PFOA, PFNA, PFHxS, PFHpA, PFTeDA, PFPeA, PFUnA, PFBA, PFBS, PFHxA. The values differ significantly, ranging from 64 ng/L to 11,223,750 ng/L, which is 175,371 times the lowest value. The PNEChum values for PFOS, PFOA, and PFNA are relatively low, at 64 ng/L, 96 ng/L, and 96 ng/L, respectively, indicating a high risk to human health that needs attention. However, the risk of PFNA is relatively low due to the small residue of PFNA in the groundwater samples. It is worth noting that the MRLs for PFHpA, PFTeDA, and PFPeA come from the model, indicating that toxicological data still needs to be studied.

Comparing the median detection concentrations with the PNEChum values shows an overall manageable situation. However, when comparing the maximum concentrations with the PNEChum values, some sampling points have significantly higher concentrations than the corresponding PNEChum values, such as PFOA, PFHxS, and PFOS, indicating a higher risk that needs to be taken seriously. Given the extensive range of PFAS compounds, attempting to regulate all of them is unfeasible. Thus, a holistic approach involving both toxicity data and exposure levels must be taken into consideration when deciding which substances should be prioritized for monitoring and control. Our results indicate that PFOA and PFOS should be given priority for monitoring and control.

Table 1. Comparison of theoretical PNEChum values and measured concentration ranges for PFAS

<table>
<thead>
<tr>
<th>CAS</th>
<th>Compound</th>
<th>MRLs (μg/kg day)</th>
<th>PNEChum (ng/L)</th>
<th>Source</th>
<th>Median (ng/L)</th>
<th>Range (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>307-24-4</td>
<td>PFHxA</td>
<td>350</td>
<td>11223750</td>
<td>ATSDR</td>
<td>4.01</td>
<td>N.D. to 1180</td>
</tr>
<tr>
<td>335-67-1</td>
<td>PFOA</td>
<td>0.003</td>
<td>96</td>
<td>ATSDR</td>
<td>8.15</td>
<td>0.05 to 4150</td>
</tr>
<tr>
<td>355-46-4</td>
<td>PFHxS</td>
<td>0.020</td>
<td>641</td>
<td>ATSDR</td>
<td>0.985</td>
<td>N.D. to 1140</td>
</tr>
<tr>
<td>375-22-4</td>
<td>PFBA</td>
<td>60.0</td>
<td>1924071</td>
<td>ATSDR</td>
<td>6.775</td>
<td>N.D. to 3610</td>
</tr>
<tr>
<td>375-73-5</td>
<td>PFBS</td>
<td>300</td>
<td>9620357</td>
<td>ATSDR</td>
<td>14.2</td>
<td>N.D. to 21200</td>
</tr>
<tr>
<td>375-85-9</td>
<td>PFHpA</td>
<td>1.43</td>
<td>45811</td>
<td>Toxtree III</td>
<td>3.675</td>
<td>N.D. to 766</td>
</tr>
<tr>
<td>375-95-1</td>
<td>PFNA</td>
<td>0.003</td>
<td>96</td>
<td>ATSDR</td>
<td>2.035</td>
<td>N.D. to 26.19</td>
</tr>
<tr>
<td>376-06-7</td>
<td>PFTeDA</td>
<td>1.43</td>
<td>45811</td>
<td>Toxtree III</td>
<td>0.64</td>
<td>N.D. to 9.21</td>
</tr>
<tr>
<td>1763-23-1</td>
<td>PFOS</td>
<td>0.002</td>
<td>64</td>
<td>ATSDR</td>
<td>2.8</td>
<td>N.D. to 145.64</td>
</tr>
<tr>
<td>2706-90-3</td>
<td>PFPeA</td>
<td>1.43</td>
<td>45811</td>
<td>Toxtree III</td>
<td>14.29</td>
<td>N.D. to 951</td>
</tr>
<tr>
<td>2058-94-8</td>
<td>PFUnA</td>
<td>3</td>
<td>96204</td>
<td>ATSDR</td>
<td>1.925</td>
<td>N.D. to 11.82</td>
</tr>
</tbody>
</table>

The total amount of PFAS in different countries and regions is shown in Table 2. In the sampling points in Liaoning, the highest total level is 26,700 ng/L, which is much higher than the concentrations listed in Table 2. There are significant differences in PFAS levels between different countries and sampling points within the same country. Due to the historical prevalence of PFAS-related industries in some areas of the United States, the groundwater in many areas contains high PFAS levels. The overall PFAS content in Asia is lower, and high-income Asian countries (such as South Korea) exhibit higher PFAS levels than South Asia and Southeast Asia, which might be linked to their industrial development levels. Although there are considerable differences in the total PFAS levels in various sampling points in China, 26 sampling points exhibit a total concentration

Figure 3. Composition of PFAS in groundwater in different regions
exceeding 50 ng/L, indicating a high level, which is attributable to China's PFAS production increase in the past two decades. This observation implies that with substantial economic and industrial growth, PFAS pollution in South Asia and Southeast Asia might shortly follow, and measures should be taken to reduce their population's exposure to PFAS.

### Table 2. PFAS concentrations in other countries and regions

<table>
<thead>
<tr>
<th>Time</th>
<th>Location</th>
<th>Total PFAS levels (ng/L)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>2015.1</td>
<td>India</td>
<td>18.7</td>
<td>[19]</td>
</tr>
<tr>
<td>2020.8</td>
<td>Korea</td>
<td>36.85</td>
<td>[20]</td>
</tr>
<tr>
<td>2021.4</td>
<td>USA</td>
<td>4773</td>
<td>[21]</td>
</tr>
<tr>
<td>2022.2</td>
<td>USA</td>
<td>1645</td>
<td>[22]</td>
</tr>
<tr>
<td>2020.1</td>
<td>USA</td>
<td>1340</td>
<td>[23]</td>
</tr>
<tr>
<td>2021.5</td>
<td>USA</td>
<td>0.33</td>
<td>[24]</td>
</tr>
<tr>
<td>2017.2</td>
<td>Vietnam</td>
<td>8.88</td>
<td>[25]</td>
</tr>
<tr>
<td>2015.3</td>
<td>Vietnam</td>
<td>21</td>
<td>[26]</td>
</tr>
</tbody>
</table>

3.4 Temporal variation in concentration levels of typical PFAS in groundwater

In this work, PFOA and PFOS were considered to be the highest-risk PFAS. Some studies have shown that PFOS and PFOA are the most abundant PFAS compounds found in the Chinese population [27]. Currently, they are classified as possible human carcinogens, and both are listed on the US Environmental Protection Agency's candidate contaminant list [28]. Therefore, it is necessary to study the annual changes in these two substances. As shown in Figure 4, the concentration of PFOS has generally decreased over the past three years, with both the maximum and median values significantly decreasing. However, the situation with PFOA is not encouraging. Although the maximum value of PFOA has decreased significantly, the overall concentration is still high. To address the issue of PFAS contamination, China's Ministry of Ecology and Environment released the second batch of key control chemical lists in 2021, which includes PFOA and PFOS, with the aim of minimizing their production and use. Therefore, the concentrations of PFOA and PFOS are expected to further decrease in the future.

4. Conclusion

This study assessed the presence of PFAS in groundwater in different regions of China. The total PFAS concentration in groundwater ranged from N.D. to 26700 ng/L. Overall, PFOA, PFBA, and PFBS have higher concentrations. There are large differences in the concentration and composition of PFAS in groundwater in different regions, which are usually related to local industrial activities and urban development. PFOA was the most prevalent PFAS component at 14 of the 39 sampling points, followed by PFBS, PFPeA, PFBA, PFOS, and PFHxA at 8, 6, 6, 3, and 2 sampling points, respectively. Due to the production and use restrictions of long-chain PFAS, short-chain alternatives such as PFBS, PFBA, PFHxA, and PFPeA are becoming mainstream. The PNEChum values of PFOS, PFOA, and PFNA are relatively low, and considering the detected concentrations, PFOS and PFOA pose a higher risk to human health, which should be taken seriously. The concentration of PFOS has decreased over the past three years, but the situation with PFOA is not encouraging. Currently, PFAS monitoring is concentrated in the eastern region, and more on-site monitoring data are needed in the western region, where groundwater is the primary source of drinking water. Furthermore, some toxicological uncertainties highlight the importance of filling the knowledge gap on PFAS toxicity. Given the high risk of some PFAS (PFOS and PFOA), regulatory and control measures are necessary.

Supporting information

Additional data and tables are available in Supporting information.

References

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