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The Distribution and Pollution Pathway Analysis of Perfluoroalkyl Acids (PFAAs) in a Typical Agricultural Plastic Greenhouse for Cultivated Vegetables

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Abstract: Plastic greenhouses play an important role in vegetable cultivation in China. While evaluations have attributed perfluoroalkyl acid contamination in greenhouse vegetables primarily to irrigation water, the potential contribution from greenhouse plastic films has consistently been overlooked, despite PFAAs' long-standing use as anti-fogging agents. In this study, a comprehensive assessment of PFAA contamination was conducted in greenhouses at the Shouguang vegetable base in China, based on extensive environmental and crop sample collection, followed by analysis using LC-MS/MS. PFAAs are still used in greenhouse plastic film, and their migration to the surface water mist and the air inside the greenhouse was also observed. Elevated levels of PFAA pollution were found near the corner areas of greenhouses with longer service times, leading to further pollution of the soil and nearby vegetables. This is considered as the primary source which may have been caused by PFAAs migrating with condensation from the plastic film and accumulating for decades. However, polluted irrigation water still remains the dominate source of PFAAs in other areas inside the greenhouse. Based on our analysis, we conclude that PFAAs present in plastic films could be the primary contaminant source for vegetables in specific zones. This underscores the urgent need for heightened vigilance towards environmental pollution within agricultural facilities, which currently represent the most prevalent mode of intensive vegetable cultivation in China.

Keywords: perfluoroalkyl acids; pollution distribution; soil contamination; plastic film; greenhouse vegetables

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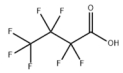
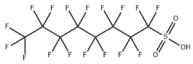
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1. Introduction

Perfluoroalkyl acids (PFAAs) have been used in industry products and daily necessities for over 60 years [1–5], and they have been released into the environment, entering the food chain and leading to human exposure [6–8]. Table 1 presents information on the fourteen PFAAs. Consequently, an increasing number of studies have focused on the problems caused by the environmental migration of PFAAs and food contamination, as well as their impact on human health [4,9–12]. It is suggested that PFAAs can bind to proteins in the blood and tissues of the human body after dietary intake, potentially causing hepatotoxicity, neurotoxicity, developmental toxicity and immunotoxicity. In recent years, research on PFAA contamination in the food chain has expanded from aquatic environments to land crops, animals, and their products [13].

Table 1. Information and basic properties of the 14 PFAAs.

No.	Abbreviated	Name	Molecular Formula	Structure Formula	CAS No.	Molecular Weight	Log *Kow*	Bolling Point (°C)
1	PFBA	Perfluorobutanoic acid	$C_4HF_7O_2$		375-22-4	214.04	/	120
2	PFPeA	Perfluoropentanoic acid	$C_5HF_9O_2$		2706-90-3	264.05	/	140
3	PFHxA	Perfluorohexanoic acid	$C_6HF_{11}O_2$		307-24-4	314.05	3.26	157
4	PFHpA	Perfluoroheptanoic acid	$C_7HF_{13}O_2$		375-85-9	364.06	3.82	175
5	PFOA	Perfluorooctanoic acid	$C_8HF_{15}O_2$		335-67-1	414.07	4.30	189
6	PFOS	Perfluorooctane sulfonate	$C_8HF_{17}O_3S$		1763-23-1	500.13	5.25	260
7	PFNA	Perfluorononanoic acid	$C_9HF_{17}O_2$		375-95-1	464.08	4.84	218
8	PFDA	Perfluorodecanoic acid	$C_{10}HF_{19}O_2$		335-76-2	514.08	5.30	218
9	PFUdA	Perfluoroundecanoic acid	$C_{11}HF_{21}O_2$		2058-94-8	564.09	5.76	160
10	PFDoA	Perfluorododecanoic acid	$C_{12}HF_{23}O_2$		307-55-1	614.1	/	245
11	PFTrDA	Perfluorotridecanoic acid	$C_{13}HF_{25}O_2$		72629-94-8	664.11	/	260
12	PFTeDA	Perfluorotetradecanoic acid	$C_{14}HF_{15}O_2$		376-06-7	486.14	/	270
13	PFHxDA	Perfluorohexadecanoic acid	$C_{16}HF_{31}O_2$		67905-19-5	814.13	/	211
14	PFODA	Perfluorooctadecanoic acid	$C_{18}HF_{35}O_2$		16517-11-6	914.14	/	235

Agricultural products contaminated with PFAAs have recently been detected in Europe, Asia, and other regions; therefore, the consuming of vegetables has been identified as an important route of dietary intake for these substances [6,13–16]. It is widely believed that water and sludge contaminated with PFAAs used for irrigation or soil amendment directly expose root systems to these chemicals which are subsequently accumulated in stems, leaves, and fruits through transpiration [13,17–19].

In recent years, the vegetable industry in China has become increasingly competitive in international markets, as export volumes exceeded 10 million tons in 2016 [20]. Agricultural plastic greenhouses that are similar to glass greenhouses have been popularly used for the cultivation out-of-season crops, particularly fruits and vegetables, due to their economic practicality [21]. Shouguang City of Shandong Province serves as China's largest greenhouse vegetable production base, boasting more than 170,000 greenhouses, where vegetable output exceeded 4.5 million tons in 2019 [22,23]. However, the presence of the large-scale fluorochemical industrial park near Shouguang City is suggested to have significantly contributed towards the PFAA pollution in the aquatic system and farmland there, as well as in the south Bohai and Yellow Seas [24–27]. Recently, PFAAs and other polyfluorinated alkyl substances (PFASs) have been reported to have been applied in anti-fog sprays and solutions for decades due to their water-repellent properties, with PFBA, PFHxA, PFHpA, and PFPeA (abbreviations defined in Table 1) being prevalent in anti-fog sprays and clothes [28]. To address the water condensation on the inner walls of

greenhouses that reduced solar incidence, anti-fogging agents containing fluorochemical compounds have been sprayed on the surface of the plastic films for thirty years [29–31].

Due to their huge output and global influence, contaminations by hazardous materials in greenhouse facilities and production have been studied and assessed. It has been suggested that greenhouse production practices increased the accumulation of trace metals, particularly Cd, Zn, Hg, and Cu in soils [21,32], as well as pesticides, antibiotics and other organic chemical pollutants due to the enclosed space [33,34]. It had also been found that phthalate esters and brominated flame retardants used in greenhouse facilities could escape and directly lead to contamination [33,35–38]. Contamination by PFAAs from greenhouse vegetable production has been appreciated and validated, but the possible contamination pathway by facilities has been ignored, which was suggested to be important for other persistent organic pollutants (POPs). Therefore, research regarding the PFAA contents and proportions in greenhouse facilities and their ability to escape has been lacking. When PFAA concentrations were detected in water, soil, and vegetable samples inside and outside greenhouses, it was suggested that irrigation water contaminated with PFAAs released by nearby chemical plants was considered the primary source [15,22].

In this study, related issues have been investigated and discussed, including the usage behavior of PFAAs for greenhouse plastic film, and the connection between the regular replacement of plastic film and PFAA loss. Therefore, a comprehensive analysis for the distribution of PFAAs in plastic greenhouse spaces and productions was performed. In addition, the primary PFAA pollution sources, pathways, and their influences also have been suggested and assessed.

2. Materials and Methods

2.1. Standards, Reagents, and Instruments

Mixed PFAA standard solutions, including 14 external standards and 11 internal standards, were purchased from Wellington Laboratories (Guelph, ON, Canada).HPLC grade acetonitrile (MeCN) and methanol (MeOH) were obtained from Fisher Scientific (Fairlawn, NJ, USA). Ammonium acetate, ammonia, hydrochloric acid, sodium chloride, anhydrous magnesium sulfate were all analytically pure and gained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Weak anion exchange solid phase extraction catridges were purchased from Waters Corporation (Milford, MA, USA). Two kinds of SinQuEChERS catridges were provided by Lumiere Technologies (Beijing, China). Centrifuge tube with different types were provided by Corning Corporation. A Waters Acquity UPLC system coupled to a Micromass Quattro Premier XE triple quadrupole mass spectrometer (Waters, Milford, MA, USA) was used to analyze the sample extracts. Separation was achieved using a Waters Acquity UPLC BEH C18 column (50 mm long, 2.1 mm i.d., 1.7 µm particles, Milford, MA, USA).

Information on the standards (including storage), the instruments and apparatus used for sample pretreatment are listed in the supporting information (SI) and Table 1.

2.2. Analytical Methods

A determination method for PFAAs in greenhouse vegetables designed by our team [39] was employed for this study (Figure S1), as well as an extraction method for PFAAs from soil and water samples based on the previous work of Chen et al. [40] and Bizkarguenaga et al. [41]. Soil samples were analyzed without being dried, yet PFAA concentrations for the vegetable and soil samples are reported on a dry weight (d.w.) basis. PFAAs in plastic films were extracted using a modified method published by Bizkarguenaga et al. [41], as well as an enrichment method of air samples collected inside the greenhouses developed by Milinovic et al. [42]. All methods above are detailed in the SI. Ultra-performance liquid chromatography (UPLC) and tandem mass spectrometry (MS/MS) was employed, as the analysis method and parameters were established by our team and published previously [39], and the mobile phases, gradient elution program, and multiple reaction monitoring parameters are provided in the SI. The quantitation limits, as well as the

operating parameters (retention time, m/z ratio, and voltage) for the target compounds are shown in Table S1. Test results of PFAA contents in soils and vegetables are expressed in the form of dry weight (d.w.).

2.3. Quality Control

To minimize contamination, fluorine-free materials were used whenever possible; however, additional quality control procedures were necessary. The isotope-labeled internal standards, matrix blanks, solvent blanks, quality control samples, and duplicate analyses as described in our previous publication were strictly followed [39]. All quality control procedures are detailed in the SI.

2.4. Description of the Plastic Film Greenhouse

A schematic of a plastic film greenhouse common in northern China is shown in Figure 1. It is typically a simple, steel-framed, arched structure approximately 100 m (east–west) by 10 m (north–south), oriented south-facing to receive maximum amounts of sunlight. The frame is covered with two layers of transparent plastic film; a thick outer film for structural stability and a thin (0.3–1.5 mm) inner film that is replaced every one to two years to maintain the anti-fogging function. The sunny side of the greenhouse is tilted, creating a low area in the southernmost portion (hereafter referred to as the "greenhouse corner"), and the soil in this area is noticeably wet as water from the inside of the plastic film continuously drips onto the surface. In this study, a motor-pumped well was employed to provide water to all 20 greenhouses by way of drip irrigation (a flexible pipe with numerous holes for seepage) that moistens the soil drop by drop as opposed to the traditional flood irrigation method. Greenhouses are typically used between September and May, during which the temperature inside is maintained at 20–30 °C and the humidity can exceed 90%, ideal conditions for out-of-season vegetables such as cucumbers, eggplants, tomatoes, and peppers.

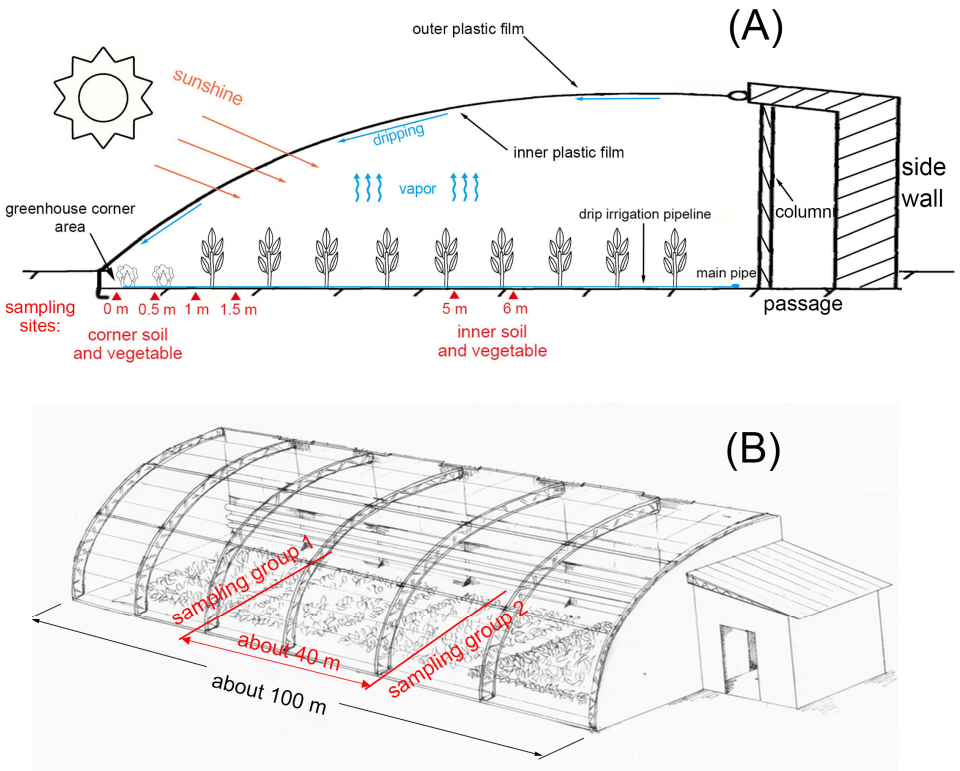


Figure 1. Typical plastic film greenhouse drawing, structure introduction and sampling point distribution. (**A**) Section view; (**B**) Side view.

2.5. Sampling Scheme

Samples were collected from twenty greenhouses in seventeen areas of eight towns in Shouguang, and sampling site distributions are shown in Figure S2. Forty-six plastic film samples were collected, including twenty from the investigated greenhouses and twenty-six purchased from the market. For the former, 1 m^2 of film was collected from the leftover materials available from each greenhouse. Two parallel groups (a north-to-south line) were arranged in each greenhouse that were separated by 40 m from east to west (Figure 1B). Soil and vegetables samples were collected from the 40 groups of 20 greenhouses, and the "corner soil/vegetable" was collected from the corner area, while the "inner soil/vegetable" was collected approximately 6 m from the greenhouse corner but still inside the greenhouse (Figure 1A). In greenhouses 13 and 16, which had significant pollution levels in the corner areas, soil samples from the corner and at distances of 0.5 m, 1.0 m, 1.5 m, 2.0 m, 3.0 m, 4.0 m, and 5.0 m from the corner were collected, as well as soil profile samples (0.25 m and 0.5 m deep) at the corner, 1.0 m, and 5.0 m sites. One air sample was collected per greenhouse in November, and a monthly dynamic monitoring program was established during the cultivation season in greenhouses 4, 9, 10, and 18, which had higher initial air PFAA concentrations. Irrigation water was collected from the entrance of the irrigation pipes. Duplicate samples were collected for each test, and the mean value was reported.

2.6. Data Analysis, Processing, and Plotting Diagrams

Based on the massive detection data listed in the SI, three types of statistical plots were employed for the results and discussion. Box plots were adopted to exhibit the species and pollution levels of the PFAAs, while a Pearson correlation analysis was utilized as a useful tool for data association finding and source identification. In addition, proportion column plots were used to visually demonstrate the consistency between the corresponding sample data. In order to ensure the accuracy and consistency of the data, 3 significant digits for data greater than or equal to 1, and 2 decimal digits for data less than 1 were rounded and reserved. The bioaccumulation factors (BAFs) for the individual PFAAs were also created and assessed in this study to find the difference in the pollution capacity between regions and species of vegetables [22]. The UPLC-MS/MS data were processed using Masslynx 4.1 software. Microsoft Excel 2007, Origin 8.0, and Adobe Photoshop CS6 Extended (13.1.2, ×64 version) software were used to plot the diagrams, draw the schematics, and annotate the figures, respectively.

3. Results

3.1. Distribution of PFAAs in the Plastic Film and Air

Currently, PFAAs are still being used as anti-fogging materials for greenhouse plastic films, making them a non-negligible pollution source. PFAAs were detected in 35 of the 46 plastic film samples, with a maximum cumulative PFAA concentration of 12.2 μg kg^{-1} (Table S2). For individual compounds, PFHxA was the most frequently detected (33 times), followed by PFOA (29 times), PFPeA (27 times), PFHpA (26 times), PFDA (25 times), and PFBA (24 times). PFOS was not found in any sample (Figure 2A). Although perfluorocarboxylic acids (PFCAs) with long carbon chains were detected occasionally, and the shorter chain PFCAs (C < 10) were the primary substances found in the greenhouse films, with PFHxA, PFOA, and PFDA present at a relatively higher content. It is notable that 11 samples had no PFAAs detected, possibly due to the use of other anti-fogging materials, such as silicon compounds [30].

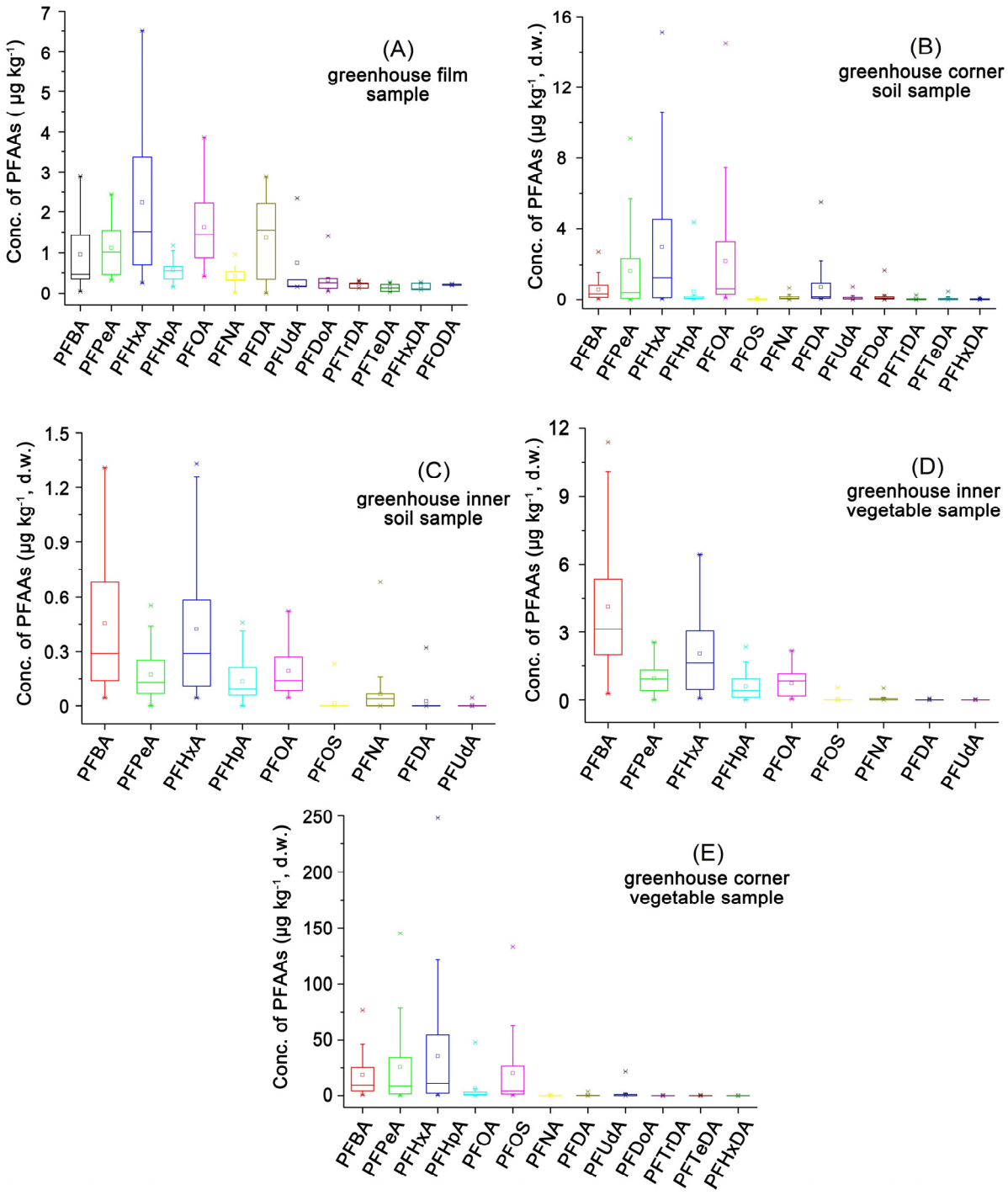


Figure 2. Distribution of PFAA concentrations in the samples of (**A**) greenhouse films, (**B**) corner soil, (**C**) inner soil, (**D**) inner vegetables, and (**E**) corner vegetables (abbreviations are defined in Table 1).

PFAAs were detected in 11 of 20 greenhouse air samples; however, only PFBA, PFPeA, and PFHxA were detected with distribution ranges of 0.13–0.22 ng m^{-3}, 0.09–0.13 ng m^{-3}, and 0.11–0.19 ng m^{-3}, respectively (Table S3). It is notable that these three have the shortest carbon chain, and therefore the lowest boiling point of all the monitored PFAAs (Table 1).

Results of the monthly dynamic monitoring showed that the substances detected in initial samples increased by a factor of 1.3–1.7 times in subsequent months, and although initially absent, some substances appeared in later months (Figure 3). Further, all detected

substances reach their maximum concentrations in February or March, followed by a rapid decrease in April and May, with some of them falling below the detection limit.

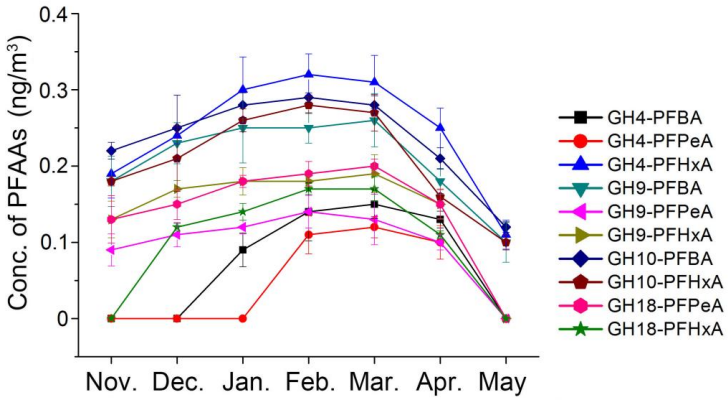


Figure 3. Dynamic changes in PFAA concentrations in greenhouse air during the cultivating season (n = 3, abbreviations are defined in Table 1).

It is indicated that PFAAs most likely escaped from the surface of the plastic film under high temperatures, high humidity, and direct sunlight conditions during the cultivation season. The short chain substances were more liable to volatilize due to their lower boiling points (i.e., higher vapor pressures), accumulate in the closed greenhouses over winter, then rapidly decrease due to ventilation in the spring. The loss of PFAAs would lead to decreased performance that would determine the plastic film replacement cycle of one to two years.

3.2. Distribution of PFAAs in the Greenhouse Soil

The greenhouse corner soils had significantly higher amounts of PFAA pollution, as PFAAs were found in all of the greenhouse corner soil samples (Tables 2 and S4). Nine greenhouses had cumulative PFAA contents greater than 15 μg kg^{-1} in the corner soil, while only seven had cumulative PFAA contents less than 5 μg kg^{-1}. The distribution of the individual PFAAs in the greenhouse corner soil samples also shows a variety of exposures, and that short chain PFAAs were dominant (Figure 2B). PFHxA and PFOA were detected in all the samples with average concentrations of 3.06 μg kg^{-1} and 2.64 μg kg^{-1}, respectively, and PFPeA and PFHpA were detected in nearly all the samples, with average concentrations of 1.92 μg kg^{-1} and 0.46 μg kg^{-1}, respectively. Although PFBA was detected in only 19 samples, its average concentration was 1.04 μg kg^{-1}. For the long chain PFAAs, PFDA was a significant polluting compound (average concentration of 1.02 μg kg^{-1}); however, PFNA, PFUdA, PFDoA, PFTrDA, PFTeDA, and PFHxDA were detected in only a fraction of the samples with concentrations typically less than 1 μg kg^{-1}. For the perfluorosulfonate acids (PFSAs), only PFOS was detected in 11 greenhouses with a concentration that ranged from 0.01 to 0.14 μg kg^{-1}, which was obviously lower than the that of PFCAs.

PFAAs were detected in all the greenhouse inner soil samples, with cumulative concentrations between 0.34 and 3.53 μg kg^{-1} and a mean value of 1.46 μg kg^{-1} (Table 2), and analysis of the individual compounds showed the inner soil samples were also short chain PFAA dominant (Figure 2C and Table S5). PFBA, PFHxA, and PFOA were detected in all forty samples, and the positive rates of PFPeA and PFHpA were both greater than 90%. Previous studies examining the soil of Shouguang greenhouses reported cumulative PFAA concentrations in the ranges of 0.57–4.00 μg kg^{-1} and 0.31–3.43 μg kg^{-1}, respectively [15,22], which were similar to the results from the inner soils in this study. However, elevated pollution at the greenhouse corner area found in this study showed significantly higher concentrations and more types of long chain compounds. In the soil samples of greenhouses 13 and 16, decreases in multiple PFAAs concentrations (initially more than 0.5 μg kg^{-1}) over the first two meters could be observed, which had stabilized over the

next three meters (Figure 4). Additionally, PFHxA, PFOA, PFDA, and PFDoA that have longer carbon chains or significantly higher initial concentrations decreased sharply within the first 1 m, while the others decreased relatively smoothly within the first 2 m. Therefore, a horizontally gradient distribution of PFAA concentrations near the greenhouse corner was observed, and it was concentration dependent and structure dependent.

Table 2. Results of concentrations of sum of PFAAs detected in greenhouse corner and inner soils and vegetables, and information on greenhouse ages, and vegetable types of all greenhouses.

Sampling No.	Greenhouse Age	Concentration of Sum of PFAAs (μg kg^{-1}, d.w.) and Vegetable Types			
		Greenhouse Corner Soil	Greenhouse Corner Vegetable	Soil Inside Greenhouse *	Vegetable Inside Greenhouse *
Sample 1, Greenhouse 1	22	18.5	320 (cabbage)	0.56	1.92 (tomato)
Sample 2, Greenhouse 1	22	9.50	102 (cabbage)	0.43	4.71 (tomato)
Sample 1, Greenhouse 2	15	8.39	67.2 (cabbage)	0.61	5.52 (tomato)
Sample 2, Greenhouse 2	15	7.95	155 (cabbage)	0.88	6.13 (tomato)
Sample 1, Greenhouse 3	5	1.32	4.67 (lettuce)	0.86	9.97 (lettuce)
Sample 2, Greenhouse 3	5	0.63	3.32 (lettuce)	0.61	6.43 (lettuce)
Sample 1, Greenhouse 4	26	23.0	198 (cabbage)	1.62	9.85 (cucumber)
Sample 2, Greenhouse 4	26	29.2	313 (cabbage)	1.33	7.61 (cucumber)
Sample 1, Greenhouse 5	15	9.27	88.5 (cabbage)	2.53	11.2 (tomato)
Sample 2, Greenhouse 5	15	11.4	205 (cabbage)	3.04	13.3 (tomato)
Sample 1, Greenhouse 6	11	1.23	22.4 (cabbage)	1.11	5.42 (pepper)
Sample 2, Greenhouse 6	11	1.46	10.7 (cabbage)	0.95	8.47 (pepper)
Sample 1, Greenhouse 7	22	7.51	27.3 (cabbage)	2.38	14.5 (cowpea)
Sample 2, Greenhouse 7	22	16.3	120 (cabbage)	2.25	16.8 (cowpea)
Sample 1, Greenhouse 8	5	1.28	14.6 (lettuce)	1.25	8.73 (lettuce)
Sample 2, Greenhouse 8	5	1.16	6.21 (lettuce)	0.57	6.27 (lettuce)
Sample 1, Greenhouse 9	7	0.52	6.58 (cabbage)	0.44	6.64 (pepper)
Sample 2, Greenhouse 9	7	0.54	3.41 (cabbage)	0.34	1.56 (pepper)
Sample 1, Greenhouse 10	11	3.78	45.4 (cabbage)	1.15	7.24 (eggplant)
Sample 2, Greenhouse 10	11	5.26	103 (cabbage)	1.46	7.55 (eggplant)
Sample 1, Greenhouse 11	10	1.94	14.9 (cabbage)	0.99	4.32 (eggplant)
Sample 2, Greenhouse 11	10	1.90	20.2 (cabbage)	0.57	3.86 (eggplant)
Sample 1, Greenhouse 12	14	3.54	26.1 (cabbage)	3.53	15.3 (pepper)
Sample 2, Greenhouse 12	14	3.45	28.6 (cabbage)	2.85	17.7 (pepper)
Sample 1, Greenhouse 13	19	7.53	122 (lettuce)	1.22	6.23 (lettuce)
Sample 2, Greenhouse 13	19	22.0	177 (lettuce)	1.52	10.4 (lettuce)
Sample 1, Greenhouse 14	11	2.72	25.8 (cabbage)	0.85	4.26 (tomato)
Sample 2, Greenhouse 14	11	4.46	30.6 (cabbage)	1.41	9.55 (tomato)
Sample 1, Greenhouse 15	21	17.3	274 (lettuce)	1.57	5.62 (lettuce)
Sample 2, Greenhouse 15	21	4.94	86.3 (lettuce)	0.86	3.10 (lettuce)
Sample 1, Greenhouse 16	26	15.5	118 (cabbage)	1.39	5.82 (rape)
Sample 2, Greenhouse 16	26	29.8	411 (cabbage)	2.37	13.4 (rape)
Sample 1, Greenhouse 17	16	4.93	71.7 (cabbage)	0.99	3.34 (tomato)
Sample 2, Greenhouse 17	16	6.78	34.7 (cabbage)	0.68	4.12 (tomato)
Sample 1, Greenhouse 18	21	18.0	185 (cabbage)	2.36	12.6 (cucumber)
Sample 2, Greenhouse 18	21	6.69	105 (cabbage)	1.83	12.7 (cucumber)
Sample 1, Greenhouse 19	19	11.9	232 (lettuce)	1.07	8.68 (lettuce)
Sample 2, Greenhouse 19	19	18.5	283 (lettuce)	2.61	9.59 (lettuce)
Sample 1, Greenhouse 20	22	15.9	164 (cabbage)	2.32	14.5 (cowpea)
Sample 2, Greenhouse 20	22	16.5	108 (cabbage)	3.01	17.3 (cowpea)

* collected at the sites about 6 m from the greenhouse corners.

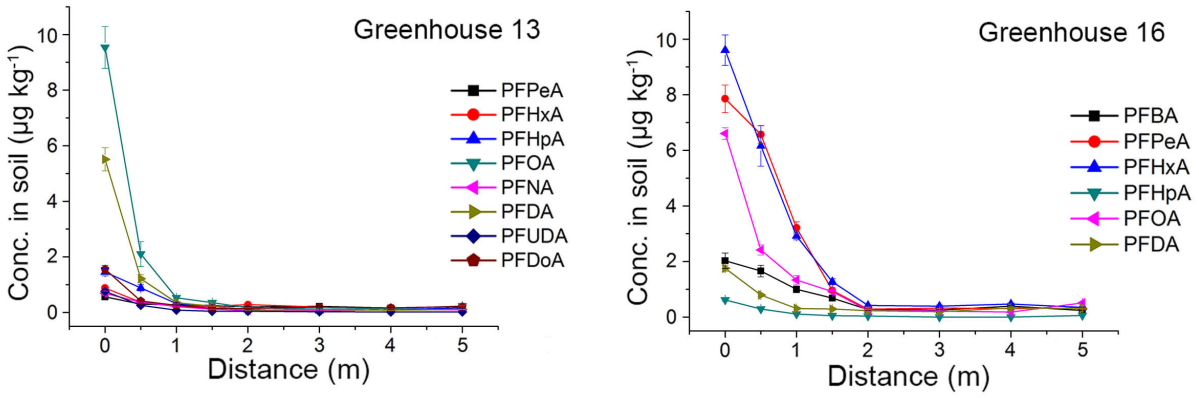


Figure 4. Horizonal gradient distribution of PFAA concentrations near the corner area of the two greenhouses (n = 3, Y axis as the distance between the sampling site and the greenhouse corner, abbreviations are defined in Table 1).

PFAAs were detected in all the samples of corner and inner soils, but notable difference could be observed. PFAA contents of the soil at the surface, 0.25 m deep, and 0.5 m deep in greenhouse 13 were 22.0, 49.1, and 26.2 μg kg^{-1}, respectively, while the corresponding data for greenhouse 16 were 29.8, 33.8, and 35.6 μg kg^{-1}, respectively. PFAA pollution from 0.25 to 0.5 m deep was elevated over samples of the surface soils (Table S6). However, the distribution of PFAAs at the four other sampling points in the greenhouses showed a decreasing trend from the top to the bottom of the profile, and samples of the same soil profiles showed similar proportions of PFAAs for the corner and inner areas (Figure S3).

3.3. Contamination in Irrigation Water and Vegetables

PFAAs were detected in all the irrigation water samples, with cumulative PFAA concentrations between 1.21 and 31.6 ng L^{-1} and a mean of 9.14 ng L^{-1} (Table S7). PFBA, PFHxA, and PFOA were detected in all water samples with concentrations between 0.17 and 14.6, 0.24 and 11.2, and 0.12 and 3.45 ng L^{-1}, respectively. PFPeA and PFHpA were detected in 17 and 15 samples, respectively, with concentrations between 0.21 and 4.64 and 0.17 and 1.87 ng L^{-1}, respectively. Conversely, PFOS, PFNA, and PFDA were detected in no more than five samples with concentrations less than 0.5 ng L^{-1} (Table S8), while none of the long chain PFAAs (C > 10) were found in any sample. Zhang et al. measured the total concentration of PFAAs in the irrigation water of the Shouguang vegetable base to be in the range of 0.58–93.4 ng L^{-1} five years before this study, with an average value of 27.8 ng L^{-1}, slightly higher than the data obtained in this study [22], indicating a decreasing trend in PFAA pollution at Shouguang City. However, the data of 5.3–615 ng L^{-1} obtained by Chen et al. [40] in Tianjin groundwater is significantly higher than the data in this study. In these two studies, the monitoring results showed that the distribution of short and medium chain substances dominated, which was consistent with the present study. However, some long-chain substances were detected in Zhang's study, which was different from the results in this paper.

A difference was noted in the PFAA contamination levels between the corner and inner vegetables (Table 2). PFAAs were detected in all the inner vegetable samples, with cumulative concentrations between 1.56 and 17.7 μg kg^{-1} with a mean of 8.56 μg kg^{-1} (Table S9). The dominant substances were short chain PFCAs that included PFBA, PFPeA, PFHxA, PFHpA, and PFOA (Figure 2D). PFBA was detected in all vegetables and had the highest concentrations, with a maximum of 11.4 μg kg^{-1} and a mean of 4.11 μg kg^{-1}. PFHxA had a mean of 2.06 μg kg^{-1}, and although they were detected in a majority of the vegetables, the means for PFPeA, PFHpA, and PFOA were all below 1 μg kg^{-1}. Further, although PFNA was detected in 45% of the vegetables at a maximum concentration of 0.54 μg kg^{-1}, most of the values were less than 0.1 μg kg^{-1}, and the mean was only 0.04 μg kg^{-1}. The detection rates and concentrations of PFOS, PFDA, and PFUDA were

even lower, while the other long chain PFCAs (C > 11) were not detected. Eun et al. conducted a study on an open field in Japan and also found that PFCAs were the main pollutants, and the exposure level of short-chain substances in vegetables was much higher than that of long-chain substances (C > 9) [43].

To take full advantage of the narrow space, some leafy vegetables like cabbage and lettuce are cultivated in the corner areas of the greenhouses. Thus, they are by-products of greenhouse production and may not necessarily be sent to market with major vegetable products. The PFAA concentration of the corner vegetables was generally higher than those from the inner areas (Figure 2E). PFHxA pollution was remarkable, with a maximum concentration of 248 μg kg^{-1} and a mean of 35.3 μg kg^{-1}, which was 39 and 17 times higher than the corresponding maximum and mean values of the inner area vegetables, respectively. PFBA, PFPeA, PFHpA, and PFOA were all detected in each sample with means of 18.9, 25.6, 6.20, and 20.5 μg kg^{-1}, respectively, that were 4.6, 27, 10, and 27 times higher than the corresponding values of the inner area vegetables, respectively. In addition, both the detection rates and mean values of PFNA and PFDA were also significantly higher than those of the inner area vegetables. Several long chain PFCAs, including PFUDA, PFDoA, and PFTrDA, that were not found in the inner area vegetables were detected in the corner vegetables, indicating a difference in the PFAA distribution in the corner versus inner samples. All the detection data for the vegetable samples can be found in detail in Tables S9 and S10. The vegetables were similar to the soil and irrigation water in that short chain PFAAs dominated the contaminant profile, especially PFOA and PFHxA.

Content levels of PFAAs in vegetables in published studies were summarized by our team [13]. For greenhouse vegetables, the sum of the contents of PFAAs in 31 greenhouse vegetables such as cucumber and tomato was measured in Zhang's study to be in the range of 1.67~33.5 μg kg^{-1} (d.w.), with an average value of 6.91 μg kg^{-1} [22]. The content level and the composition structure were close to the result range of 40 inner vegetable samples in this study. However, the pollution level was sharply lower than that of vegetables from 40 corner vegetable samples.

4. Discussion

4.1. PFAA Pollution Features

It has been suggested that the molecular structure can affect the migration capacity of PFAAs, and ones with shorter carbon chains tend to transfer with water, yet ones with longer carbon chains tend to combine with soil organic matter (SOM), and this fact was employed to explain the pollution features in this study [13]. First, the shorter chain PFAAs were dominant in the soil, vegetable, and irrigation water samples, as shown in Figure 2, and this was in accordance with published studies [15,22,43]. Second, the horizontal gradient distribution near the greenhouse corner could also be explained, as it has been reported that PFAAs can migrate and diffuse in soil from high-concentration pollution centers (sources) and have gradient distributions of tens of kilometers near fluorine chemical plants [26,44]. However, the various profile distribution features of PFAAs would be caused by the transmittal downward in the soil column through the infiltration of water, including irrigation water [22,43].

For the vegetables, the BAFs generally decreased with the increasing length of the PFAA carbon chain for both the corner and inner area vegetables (Figure S4), also indicating a relationship between bioaccumulation capacity and molecular structure. This is consistent with previous works where PFBA always had the highest BAFs followed by PFPeA, PFHxA, PFHpA, PFOA, and the long chain PFAAs [13]. Additionally, the PFAAs showed a higher bioaccumulation ability in leafy vegetables than in fruit vegetables, possibly due to the transportation force of transpiration [13,45,46]. Therefore, the gap of the pollution level between the leafy vegetables from the greenhouse corner area and the fruit vegetables from the other areas in the greenhouse was greater.

4.2. Plastic Film–Corner Soil–Vegetable Pollution Pathway

As anticipated, cumulative PFAA concentrations in the corner soils exhibited significant positive correlation (R^2 = 0.797, $p < 0.01$) with the vegetables (Figure 5A). Further, ten groups of samples with the highest PFAA levels in the corner vegetables were analyzed, and the PFAA proportion in most groups was more closely related to the corner soils than the inner area vegetables (Figure 6A). Although the difference observed in greenhouse 19 was not significant, pollution levels of PFBA and PFHpA of the inner area vegetables were higher, but that of PFPeA was lower. These findings indicated the highly polluted soils as the dominant pollution source.

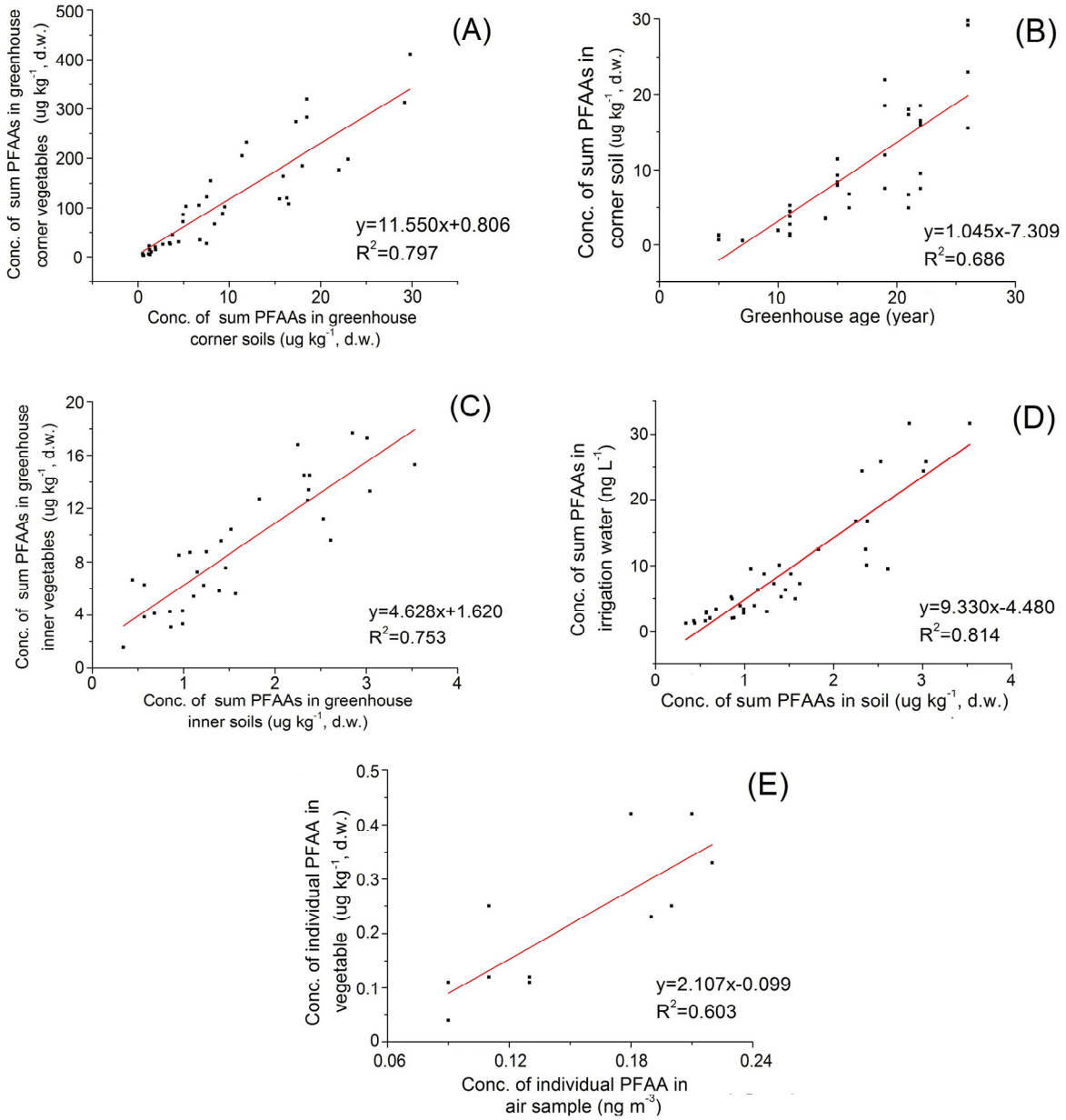


Figure 5. Correlation analysis of sum of PFAA concentrations for different samples. (**A**) Corner vegetable vs. corner soil; (**B**) Corner soil vs. greenhouse age; (**C**) Inner vegetable vs. inner soil; (**D**) Irrigation water vs. inner soil; (**E**) Vegetable vs. air samples.



Figure 6. Comparison of PFAA proportions in relative samples (abbreviations are defined in Table 1).

So, where did the massive PFAA amounts in the corner soil samples come from? There was no correlation in the cumulative PFAA concentrations between the corner soil and the greenhouse plastic film according to a comparison of the data in Tables S3 and S5;

however, a significant difference related to greenhouse age was demonstrated. The ages of 20 greenhouses ranged from 5 to 26 years (Table 2), and according to Pearson correlation analysis, the cumulative PFAA concentrations of the corner soils showed a positive linear correlation (determination coefficient of 0.686 at $p < 0.01$) with greenhouse age (Figure 5B).

Considering PFAAs are widely applied in greenhouse plastic film production, a possible pollution pathway was inferred as follows. Most of the PFAAs released from the plastic film migrated via condensation water that flowed to the greenhouse corner soil, accumulated there, and then diffused and infiltrated the soil for decades. This process led to the elevated contamination. As long-term migration tests and early plastic film sampling analysis are impossible to conduct, this is a reasonable inference.

4.3. Irrigation Water–Soil–Vegetable Pollution Pathway

Irrigation water was previously considered to be the primary source of contamination for greenhouse vegetables [22]. In this study, the cumulative PFAA concentrations in the vegetables from the greenhouse inner area and their corresponding irrigation waters showed a significant positive correlation ($R^2 = 0.814$, $p < 0.01$), as did the vegetables and their corresponding soils ($R^2 = 0.753$, $p < 0.01$) (Figure 5C,D). In addition, the proportion of PFAAs for the irrigation waters compared to the inner soils and vegetables was similar, as seen in the seven greenhouses with the highest contaminations in inner vegetables (Figure 6B). However, the proportion of long chain PFCAs was generally lower in vegetables than in soils ($p < 0.05$), while the short chain PFCAs, especially PFBA, exhibited the opposite trend ($p < 0.01$) due to different bioaccumulation capacities.

To determine if irrigation water polluted the greenhouse corner area, ten groups from five greenhouses with the least contaminated corner vegetables were selected to compare the PFAA proportions of the corner soil, corner vegetables, inner vegetables, and the irrigation water samples. Nine of the groups showed consistent compositions between the irrigation water, inner vegetables, and corner vegetables, with the obvious difference being the corner soil (Figure 6C). In the remaining group (11-2), although the composition of the corner vegetables was different from that of the inner vegetables, it was similar to that of the irrigation water. These results confirmed irrigation as a source of pollution for greenhouse vegetables, and when PFAA pollution in the corner soil was close to that of the inner soil, the irrigation water was the primary pollution source.

4.4. Plastic Film–Air–Vegetable Pollution Pathway

Analysis of the data reveals a correlation between the PFAAs detected in the air and in the plastic film of the same greenhouse (Tables S2 and S3; Figure S5). All the substances detected in the air had relatively higher contents in the corresponding plastic film ($p < 0.01$), with individual substances ranging from 1.22 to 5.87 μg kg^{-1}. In contrast, substances that were not detected in the greenhouse air had corresponding concentrations of less than 1.5 μg kg^{-1}. Thus, it can be inferred that the presence of PFBA, PFPeA, and PFHxA in the plastic films directly affects their distribution in the greenhouse air. Therefore, eleven sets of data were screened for substances that were detected both in the vegetables and air samples. A positive correlation ($R^2 = 0.603$, $p < 0.01$) between the data (Figure 5E) suggests that short chain PFAAs in the greenhouse air may be a pathway for the contamination of the vegetables, yet the pollution capacity is relatively limited.

4.5. Feasible Pollution Control Measures

It is necessary to conduct pollution control and the remediation of PFAAs in greenhouses. We think some measures are possible and worth considering. As leafy vegetables planted near the polluted greenhouse corner area have a stronger bioaccumulation capacity, they can be used for soil bioremediation, but a harmless treatment method needs to be developed. In addition, the industry of agricultural plastic film production also needs to attach importance to this environmental pollution problem and further improve the anti-fogging production process by possibly using silicon-based compounds as substitutes.

Additionally, purification of the irrigation water by any material is feasible. Several studies have suggested a water removal solution and effective adsorption materials for PFAAs, including the use of resin exchange and activated carbon [47–50].

5. Conclusions

Currently, PFAAs are still being used as anti-fogging materials for greenhouse plastic films, making them a non-negligible source of pollution. PFAAs are likely to escape from the surface of the plastic film under high temperatures, high humidity, and direct sunlight conditions during the cultivation season. The short chain substances are more prone to volatilization due to their lower boiling points (i.e., higher vapor pressures), accumulating in closed greenhouses over winter and then rapidly decreasing due to ventilation in the spring. The loss of PFAAs would result in decreased performance that determines the replacement cycle of plastic film, which is typically one to two years. However, elevated levels of PFAA pollution were found near the corner areas of greenhouses with longer service times. This may be caused by PFAAs migrating with condensation from the plastic film and accumulating over decades. Consequently, this leads to the further diffusion and pollution of soil and vegetables in certain nearby areas, with PFAAs being identified as the primary contamination source. In other areas within a greenhouse, irrigation water polluted by nearby industry emissions was considered as the dominant source of contamination based on previous finding and reports. On contrast, there is limited risk for vegetable pollution through air pathways; however, further research is required on this aspect.

The inference of plastic film as the source of PFAAs and their potential migration into the corner soil and vegetables within greenhouses were innovative findings in this study and serve as a reminder of the need to consider the potential sources of POPs in agricultural facilities and to further study their possible migration and contribution to crop pollution. This is paramount for the sustainable development of environmental science and food safety. Additionally, the greenhouse space and irrigation water of the Shouguang vegetable base still faces persistent contamination risk due to PFAAs, and this requires us to consider several measures, such as reducing industrial emissions, performing soil remediation, and conducting the real-time purification of irrigation water, as well as decreasing PFAA applications in plastic film products.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/agriculture14081321/s1, Figure S1: Graphical introduction for determination of PFASs from vegetables [39]; Figure S2: Distribution of sampling sites at Shouguang City, China; Figure S3: Comparison of PFAAs concentration in ground soil samples with different sampling positions in parallel groups from 4 greenhouses (GH). (μg kg^{-1}, d.w.); Figure S4: Box chart distribution of bioaccumulation factors (BAFs) of PFAAs in inner vegetables and corner vegetables; Figure S5: Correlation analysis of PFAAs concentration in air samples and plastic films; Table S1: Parameters of all substances for MS analysis and MQLs in all matrixes [39]; Table S2: Concentration of PFAAs in all greenhouse plastic film samples (n = 2); Table S3: Concentration of PFAAs in the air samples inside of greenhouse (n = 2); Table S4: Results of individual contents of PFAAs detected in greenhouse corner soil samples (n = 2); Table S5: Results of individual contents of PFAAs detected in greenhouse inner soil samples (n = 2); Table S6: Detection and additive results of PFAAs in profile soils (ground, 0.25 and 0.5 m depth) of different sampling places in two greenhouses (n = 2); Table S7: Concentration of PFAAs in irrigation water from the wells for each greenhouse (n = 2); Table S8: Results of individual contents of PFAAs detected in greenhouse inner vegetable samples (n = 2); Table S9: Results of individual contents of PFAAs detected in greenhouse corner vegetable samples (n = 2); Table S10: All the data of BAFs in this study.

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