



Article Accumulation and Transport of Phthalic Acid Esters in the Soil-Plant System of Agricultural Fields with Different Years of Film Mulching

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Abstract: In this study, we investigated the accumulation and transport patterns of phthalate ester (PAEs) compounds in the soil-plant system of maize and cabbage fields under different film mulching years. The total content of five PAEs in the maize fields soil ranged from 156.19 to 566.1 μ g kg⁻¹ with film mulching for 0–20 years. The total content of five PAEs in the cabbage field soils ranged from 252.48 to 559.07 μ g kg⁻¹ with film mulching for 0–30 years. The PAEs content in cabbage and maize field soils was lower than the environmental quality standards for soil (GB 15618-2008). With the increase in film mulching years, both maize and cabbage soil PAEs contents increased significantly (p < 0.05), while among the five PAEs, the contents of di-n-butyl phthalate (DnBP) and di(2-ethylhexyl) phthalate (DEHP) increased the most significantly, and the content of DEHP in the soils was the highest. The DEHP content in soils planted with maize ranges from 134.03 to 406.79 μ g kg⁻¹ with the film mulching for 20 years; while in soil planted with cabbage, it ranges from 229.35 to 405.2 μ g kg⁻¹ with the film mulching for 30 years. The DEHP content in all of the soils has not exceed the limit value established by the USEPA in U.S. Five PAEs were detected in maize seeds and cabbage leaves, among which the DEHP content exceeded the maximum residue limit set by the National Food Safety Standard (GB 9685-2016) for DEHP in food after more than 10 years of mulching. The bioaccumulation and translocation factors in cabbage showed a significant positive correlation with the film mulching years. However, the bioaccumulation factor and translocation factor in maize have weak correlations with the film mulching years, possibly due to the lower PAEs content in the deep soil layers where maize roots are distributed. Our research revealed a significant association between the presence and distribution of PAEs in crops and mulching years. These novel discoveries provide fundamental information for controlling PAEs pollution in agricultural environments.

Keywords: accumulation; transport; phthalic acid esters; different film mulching; cabbage; maize; soil

1. Introduction

The plastic film mulching technique was introduced in China in the late 1970s [1]. It has significantly promoted agricultural production by conserving water, suppressing weed growth, increasing soil temperature, and enhancing cold resistance. Therefore, this technique has considerably enhanced crop yield and water use efficiency [2]. Studies have shown that plastic film mulching could increase grain and cash crop yields by 20–35% and 20–60%, respectively [3]. However, the incomplete recovery of the plastic film has resulted



Citation: Zhang, H.; Li, J.; Ma, T.; Ma, K.; Ni, X.; Wu, S. Accumulation and Transport of Phthalic Acid Esters in the Soil-Plant System of Agricultural Fields with Different Years of Film Mulching. *Sustainability* **2023**, *15*, 15589. https://doi.org/10.3390/ su152115589

Academic Editor: Teodor Rusu

Received: 22 September 2023 Revised: 22 October 2023 Accepted: 26 October 2023 Published: 3 November 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). in its residue remaining in agricultural soils. The presence of plastic residues in the soil not only affected the transport of water and nutrients but also hindered gas movement, decreased soil permeability, and affected crop root growth and the uptake and utilization of water and fertilizers, leading to a decline in crop yield [4].

During the process of plastic film production, plastic films were often supplemented as plasticizers to enhance their chemical stability, flexibility, transparency, and other properties of plastic films [5,6]. Studies have indicated that PAEs can constitute up to 80 wt% of the plasticizers used in China [7,8]. Residual plastic films in the soils could also release pollutants, such as PAEs, into the soils [9]. PAEs are a class of organic compounds found in plastic films that are difficult to degrade and toxic [10]. These accumulated poisonous pollutants in the soil could be transported into surface water and groundwater through precipitation and surface runoff. They also would be emitted into the atmosphere through volatilization, indirectly causing water and air pollution [11]. They may also act as endocrine disruptors [12], posing potential health risks to humans and other organisms [13].

PAEs compounds are generally added to plastic products physically without forming chemical bonds with the polymer components [14]. This makes them prone to being released into the environment during the production, storage, use, and disposal of plastic products, leading to severe pollution [15,16]. PAEs have potential adverse effects, and the United States Environmental Protection Agency has identified butyl benzyl phthalate (BBP), di(2-ethylhexyl) phthalate (DEHP), dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DnBP), and di-n-octyl phthalate (DOP) as "Priority Toxic Pollutants", refs. [2,6,17,18], and specific soil pollution control and management standards have been established. DMP, DBP, and DOP are also included in the priority control pollutant black list in China [19].

With the extensive and long-term use of plastic film mulching, the soil residue from plastic films has become an important problem affecting soil and food safety [2]. Due to improper recycling cycles, the accumulation of PAEs in the soil becomes more serious [20]. In the Pearl River Delta region, the total amount of PAEs in vegetable soils can reach up to 46,000 μ g kg⁻¹ [21]. PAEs have been widely detected in soil, vegetables, fruits, and grains [2,22–25]. The contents of PAEs in soils and plants were reported from 465 to 5450 μ g kg⁻¹ dw (dry weight), and from 2440 to 21,800 μ g kg⁻¹ dw in Dalian, China, respectively, [26]. It is widely believed that plants can absorb and accumulate phthalates in agricultural soils [27–29].

However, in the context of specific ecological factors and soil physicochemical properties in arid ecosystems, the rate of residual plastic films in agricultural soils, as well as the accumulation and transport of PAEs in the agro-soil-plant system, have not been thoroughly investigated [30–33]. Ningxia is one of the main provinces in China where plastic mulching is extensively used. Especially, the large-scale demonstration of plastic film-mulched maize and cabbage planting techniques has led to an annual increase in plastic mulch usage. By selecting these two typical crops in Ningxia, China, the aim is to investigate the transport and accumulation of PAEs in these two crops and obtain a comprehensive understanding of their potential risks and impacts in the dryland agricultural region.

Therefore, the major objectives of this paper were: (1) to analyze the dynamic change of PAEs contents in soils with different mulching years; (2) to explore the accumulation and transport of PAEs in cabbage and maize plants under different mulching years; (3) to explore the accumulation and transport patterns of PAEs derived from plastic film degradation agro-soil-plant system; (4) to provide a theoretical basis for assessing the acumulative risks of PAEs in soils and crops, evaluating the environmental effects of plastic film mulching and ensuring its safe use.

2. Overview of the Study Area

According to the survey and monitoring of plastic film residues in Longde County, the dryland agricultural region of Ningxia Hui Autonomous Region, China, in 2020, had a history of plastic film usage for 30 years. The predominant cropping patterns in this

region include crop rotation and monoculture. The primary purposes of using plastic film mulching are moisture retention and temperature increase, with a film thickness of 0.012 mm for maize and 0.008 mm for vegetable crops. The plastic film residues are mainly distributed in the top 0–20 cm of soil, accounting for 44.31–92.74% of the total residue amount. And about 7.26–55.69% of the total residue amount in the 20–30 cm soil layer. The soil type in the monitored area is loam. Irrigation is mainly dependent on rainwater.

3. Materials and Methods

3.1. Sample Collection

In August 2020, mature maize plants and cabbage samples, as well as rhizosphere field of the relevant crops, were collected from the planting base in Longde, China (coordinates: 105.972222° E, 35.680833° N). Each sampling plot had a size of 1×1 m. Stainless steel shovels collected soil samples from the 0–20 cm depth. Five sampling points were randomly chosen in a plum blossom-shaped distribution in the selected experimental site. The samples from each sampling point were mixed using the composite sampling method. And the impurities, such as stones, dry branches, and leaves, were cleaned. There were 3 repeated sampling plots in each treatment of different film mulching years. A quartering method was employed, and 1 kg of soil sample was stored in cloth bags to avoid contact with plastic materials and transported to the laboratory. The soil samples were air-dried, and plant roots and plastic film were removed. The remaining soil was sieved through a 1 mm mesh and stored in sealed bags. Before analysis, the samples were stored at 4 °C. The cabbage and maize samples were rinsed with deionized water, freeze-dried, and ground using a stainless-steel grinder. The finely ground samples were stored at -20 °C before analysis. The cabbage and maize samples grown in agricultural fields without plastic mulching were selected as the control group (CK) to study the accumulation and translocation of PAEs in plants. The soil samples without plastic mulching were chosen as the control group (CK) to investigate the accumulation of PAEs in the soil. A total of 12 cabbage soil samples were collected from different mulching years (CK, 10, 15, and 30 years), with 6 samples each of cabbage roots and leaves. Additionally, 12 maize soil samples were collected from different mulching years (CK, 5, 10, and 20 years), along with 12 samples each of maize roots, stems, leaves, and grains.

3.2. Sample Treatment

According to the method proposed by Li et al. [34], the detection method used was gas chromatography-mass spectrometry (GC-MS). We accurately weigh 2 g of cabbage root samples and 5 g of the other samples and put them into 50 mL centrifuge tubes. We added 20 mL of acetone: n-hexane (1:1, v/v) mixture (n-hexane is chromatographic grade, acetone is analytical grade) to the tubes. We let it stand overnight, then ultrasonic extraction was performed for 30 min. The mixture was centrifuged at 4000 rpm for 5 min and the supernatant was transferred to new centrifuge tubes. The bottle was quickly placed in the refrigerator for cold storage. The above steps were repeated twice for the remaining samples by adding 20 mL of the acetone-n-hexane mixture. The combined 60 mL supernatant was concentrated using a rotary evaporator at 30 °C to a volume of 1–2 mL. We added 5 mL of n-hexane to exchange acetone, and further concentrated the solution to less than 1 mL. The solution was filtered through a 0.22 mm membrane glass filter, then transferred the solution to a brown sample bottle and diluted with n-hexane to a final volume of 1 mL.

3.3. Analysis Conditions

Qualitative and quantitative analysis was performed using a Shimadzu GC-MS QP-8040 triple quadrupole gas chromatography-mass spectrometry system (Shimadzu, Kyoto, Japan) equipped with an Rtx-5MS quartz capillary column (30 m \times 0.25 mm \times 0.25 µm). The chromatographic conditions were as follows: High-purity helium gas was used as the carrier gas at a flow rate of 1 mL/min, with a sample injection volume of 1 µL in splitless mode. The injection port temperature was set at 280 °C, and the oven temperature was maintained at 70 °C. The temperature program was as follows: hold at 70 °C for 1 min, increase at a rate of 15 °C/min to 200 °C and hold for 2 min, increase at a rate of 5 °C/min to 220 °C and hold for 5 min, increase at a rate of 5 °C/min to 250 °C and hold for 5 min, and finally increase at a rate of 15 °C/min to 300 °C and hold for 5 min.

The mass spectrometry conditions were set as follows:

The ion source temperature was 250 °C.

The interface temperature was 280 °C.

The solvent delay time was 3 min.

Compound quantification was performed using the selected ion monitoring (SIM) mode.

The target compounds of PAEs in the sample, including DEP, DMP, DnBP, BBP, and DEHP, were determined by GC-MS analysis.

3.4. Data Analysis

Graphs were generated using OriginPro 2023 software. Statistical analysis of the data was performed using SPSS 26.0. One-way analysis of variance (ANOVA) was conducted to analyze the differences in the levels of PAEs in cabbage and maize soil with different mulching years, as well as the levels of PAEs and their congeners in maize roots, stems, leaves, and grains with varying years of planting. Duncan's multiple comparison test was used to assess the significance of the differences (p < 0.05).

To compare the enrichment and translocation abilities of PAEs, the bioconcentration factor (*BCF*) and translocation factor (*TF*) were calculated. BAF includes the root concentration factor (*RCF*), stem concentration factor (*SCF*), leaf concentration factor (*LCF*), and grain concentration factor (*GCF*) [28]. RCF, SCF, and LCF indicate the ability of plants to absorb compounds from the soil in different organs and can be calculated as follows:

$$RCF = \frac{C_{root}}{C_{soil}} \tag{1}$$

$$SCF = \frac{C_{stem}}{C_{soil}} \tag{2}$$

$$LCF = \frac{C_{leaf}}{C_{soil}} \tag{3}$$

$$GCF = \frac{C_{grain}}{C_{soil}} \tag{4}$$

The translocation factor (*TF*) [28] was used to assess the ability of plants to transfer organic chemicals from the roots to other parts. It is defined as follows:

$$TF_{stem} = \frac{C_{stem}}{C_{root}}$$
(5)

$$TF_{leaf} = \frac{C_{leaf}}{C_{root}} \tag{6}$$

$$TF_{grain} = \frac{C_{grain}}{C_{root}} \tag{7}$$

where C_{root} , C_{stem} , C_{leaf} , C_{grain} , C_{soil} represent the concentrations (µg kg⁻¹) of the compound in the roots, stems, leaves, grains, and soil, respectively.

Pearson correlation analysis was used to observe the relationship between several factors and the physical-chemical parameters of PAEs. And the correlation heatmap was generated using the "origin 2023" software.

4. Results and Discussion

4.1. Influence of Different Mulching Years on the Accumulation of PAEs in Soil

Significant differences were observed in the soil PAEs content between cabbage and maize fields with different mulching years (Figure 1). The highest content of five PAEs in the soil of a maize field with 20 years of mulching was 566.10 μ g kg⁻¹, while in a cabbage field with 30 years of mulching, the highest content of five PAEs in the soil was 559.07 μ g kg⁻¹. The PAEs content in the cabbage field's soil was lower than that in the maize field. With the increase in mulching years, the PAEs content in maize and cabbage fields significantly increased (p < 0.05). Among the five PAEs congeners, DnBP and DEHP showed the most significant increase, with DEHP having the highest content. The DEHP content in the soil of the maize field with 0-20 years of mulching ranged from 134.03 to 406.79 μ g kg⁻¹ (Figure 1a), while in the cabbage field with 0–30 years of mulching, the DEHP content ranged from 229.35 to 405.23 μ g kg⁻¹ (Figure 1b). According to the soil cleanup guidelines of the New York State Department of Environmental Conservation, the DEHP allowable 4350 μ g kg⁻¹ [35]. These DEHP in all soils in the present study did not exceed the limit values (4350 μ g kg⁻¹). The Chinese Soil Environmental Quality Standard (GB 15618-2008) [36] designates six PAEs as soil pollutants (DMP, DEP, DBP, DOP, DEHP, and BBP), with a minimum allowable concentration of 5000 μ g kg⁻¹ in agricultural soil [4]. In the agricultural soils of the study area, the highest PAEs content in the soil for growing maize was 566.10 μ g kg⁻¹, while the highest PAEs content in the soil for growing cabbage was 559.07 μ g kg⁻¹. Moreover, both values were found to be below the environmental control standard limit (5000 μ g kg⁻¹) for PAEs in Chinese agricultural soils.



Figure 1. Contents of PAEs and their congeners in soils with different mulching years of plastic film: (a) for soil planted with maize; (b) for soil planted with cabbage. Different lowercase letters indicate significant differences between treatments (p < 0.05).

Studies have shown that PAEs in the soil can originate from atmospheric deposition, sewage irrigation, sludge application in agriculture, the use of fertilizers, manure, and pesticides, as well as the degradation of agricultural plastic films and plastic waste by rainwater [37]. It is generally believed that compounds with larger molecular weights and higher Kow values exhibit stronger hydrophobicity, greater adsorption capacity in the soil, and more excellent resistance to desorption and aging. The logKow values of DnBP and DEHP are 4.45 and 7.5, respectively [16], indicating their strong lipophilicity and high octanol/water partition coefficients, making them readily adsorbed by soil and difficult to degrade or disappear through other pathways, leading to their high accumulation in organisms through the food chain. Due to their large molecular weights and Kow values, DEHP and DnBP tend to have higher residual levels in the soil [38]. Moreover, DEHP has a higher molecular weight than DnBP, suggesting that DEHP has a more substantial adsorption capacity in soil than DnBP. Our research has found that the levels of DEHP

in the agricultural soil of maize and cabbage fields under different mulching years are significantly higher than the levels of DnBP (Figure 1). Other congeners of PAEs, with higher water solubility, smaller octanol/water partition coefficients, and molecular weights, are more prone to biodegradation in soil, resulting in lower residual levels. Li [35] conducted a survey on the levels of PAEs in 36 plastic mulched vegetable fields in the Shandong Peninsula. The results indicated that DnBP and DEHP were the dominant homologs in the study area. Soil monitoring of maize and cabbage cultivation revealed higher levels of DEHP and DnBP, along with lower levels of other PAEs congeners, consistent with previous research findings [26,39].

The study found that microorganisms in the soil are capable of partially degrading PAEs in the soil, and a portion of PAEs can volatilize into the atmosphere [14]. Our study revealed a significant increase in PAEs levels in the soil of cabbage and maize fields with increasing mulching years (Figure 1), the difference compared to the control was significant. The aging of microplastics in the soil and longer mulching years can exacerbate the binding of PAEs with soil organic components, leading to their long-term accumulation in the soil.

The study found that the levels of BBP, DEP, and DMP in the soil of maize and cabbage fields did not exhibit a linear increase with the increasing of mulching years (Figure 2). This could be attributed to the behaviors during the process of PAEs entering the soil environment, including volatilization, leaching, degradation, aging, binding with soil solids and transport to organisms, or uptake by plants and removal from the farmland [14,40,41]. These processes can lead to a gradual decrease in the PAEs content in the topsoil. Short-chain PAEs compounds, such as BBP, DEP, and DMP, due to their higher water solubility and smaller octanol/water partition coefficients, are more prone to degradation, resulting in non-linear residual levels in the soil with the extension of mulching duration.





Comparing the soils of maize and cabbage cultivation, it can be observed (Figure 3) that the PAEs content in soil planted with maize is higher than that in soil planted with cabbage under the same mulching years. The possible reasons are as follows: Firstly, vegetable fields are typically covered with plastic film for 1–2 months, while maize fields are covered for as long as 10 months. The longer the plastic film remains in the soil of maize fields, the higher the residual amount, and consequently, the higher the PAEs content; secondly, cruciferous crops like cabbage have higher enrichment capacity of PAEs than crops from other families, leading to a higher transport of PAEs from the soil to the plant organs. Long-term use of plastic mulch and the accumulation of residual films can increase the PAEs content in the soil, thereby increasing the risk of soil pollution and posing a threat to human health.



Figure 3. Contents of PAEs in soil planted with maize and cabbage under different mulching years.

4.2. The Accumulation of PAEs in Plant Organs

Analyzing the accumulation of PAEs in cabbage, particularly in the roots (Figure 2), the PAEs content in cabbage roots with mulching is higher than that in uncovered plastic film soil, indicating that cabbage roots can absorb and accumulate PAEs from the soil. The PAEs content in cabbage roots is higher than that in the leaves, suggesting that PAEs are more prone to accumulate in cabbage roots, and there are significant differences in PAEs content among different mulching years. Four compounds, DEHP, DMP, DEP, and DnBP, were detected in the roots, with DEHP having the highest concentration, followed by DnBP, DEP, and DMP. Five compounds, namely BBP, DEHP, DMP, DEP, and DnBP, were detected in the leaves and soil, with DEHP and DnBP having the highest concentrations. According to the National Food Safety Standard (GB 9685-2016) [42], the maximum allowable residue limit for DnBP and DEHP in food is 300 and 1500 μ g kg⁻¹, respectively. In the leaves of cabbage with 30 years of mulching, the DnBP content is 349.68 μ g kg⁻¹, exceeding the maximum allowable residue limit in food set by the National Food Safety Standard $(300 \ \mu g \ kg^{-1})$, which indicated a safety risk for intake. The DEHP content in cabbage leaves is 1786.05 μ g kg⁻¹, with the 10 year of mulching, 2843.28 μ g kg⁻¹ in the 15th year, and 4100.00 μ g kg⁻¹ in the 30th year. All of them had exceeded the maximum allowable residue limit in food set by the National Food Safety Standard (1500 $\mu g kg^{-1}$). The exceedance rates are 19.07%, 89.55%, and 173.3%, respectively. Therefore, the consumption of these vegetables would have certain health risks.

The levels of DEP and DMP in cabbage roots showed an initial increase followed by a decrease with the extension of mulching years (Figure 4a,b). In contrast, DnBP, DEHP, and total PAEs significantly increased with the extension of mulching years (Figure 4c,e,f). The DEP content in cabbage leaves was lower in the 15th year of mulching than in the 10th year but higher than in the 30th year (Figure 4a). DMP exhibited a significant increase in the 0–15 years of mulching and was not detected in the 30th year (Figure 4b). The pollutant concentrations in cabbage leaves may be influenced by atmospheric deposition rather than solely absorption and translocation from the soil. Several studies have indicated that vegetables can absorb and accumulate PAEs from soil and air sources [43,44]. The contribution of PAEs from atmospheric deposition to PAEs in field/farm vegetables needs to be clarified and requires further research.



Figure 4. Contention of PAEs in the organs of cabbage under different mulching ages of plastic film: (a) for DEP in the organ of cabbage; (b) for DMP in the organ of cabbage; (c) for DnBP in the organ of cabbage; (d) for BBP in the organ of cabbage; (e) for DEHP in the organ of cabbage; (f) for PAEs in the organ of cabbage. Different lowercase letters indicate significant differences between treatments (p < 0.05).

Analysis of the enrichment of PAEs in maize (Figure 5f) shows that the concentration of PAEs in the soil is the lowest, only 156.19 μ g kg⁻¹. The concentrations in maize roots, stems, leaves, and grains are relatively higher, ranging from 3.24 to 10.95 times more than that of the soil concentration. This indicates that maize can absorb and accumulate PAEs in its organs. The concentrations of PAEs in different maize organs are as follows: leaves > stems > roots > grains. DEHP, DMP, DEP, and DnBP were detected in all of the maize and soil, while BBP was only detected in some soil and maize organs. DEHP had the highest residue levels in both soil and maize, while DMP had the lowest in both soil and plants. Based on the relevant control standards for DnBP and DEHP in food set by the Chinese Ministry of Health, the concentrations of DnBP and DEHP in maize grains exceeded the permissible limits after 10 and 20 years of mulching.



Figure 5. Contention of PAEs in the organs of maize under different mulching ages of plastic film: (a) for DEP in the organ of maize; (b) for DMP in the organ of maize; (c) for DnBP in the organ of maize; (d) for BBP in the organ of maize; (e) for DEHP in the organ of maize; (f) for PAEs in the organ of maize. Different lowercase letters indicate significant differences between treatments (p < 0.05).

Therefore, the PAEs content in maize grains does not meet the edible standards after the mulching period exceeds ten years. It is recommended to strengthen the recovery of residual film and reduce the mulching period to prevent the aging and degradation of mulch film. The concentration of PAEs in maize organs does not correlate with the mulching years in roots, stems, and leaves.

The average concentration of PAEs in maize leaves with a plastic film mulching of 0–20 years is the highest (Figure 5f). Studies have shown that leaves serve as the primary storage compartment for these compounds [14]. Leaves are known to easily absorb organic pollutants from the air [43], highlighting the importance of the air absorption pathway. A previous study confirmed that a single plant of *B. hispida* gourd with a fruit was able to accumulate more than 700 mg of DEHP when exposed to DEHP-contaminated air for 6 weeks [45]. Among the PAEs in maize leaves, the content of the homolog DEHP is the highest (Figure 5e), as leaves have a greater absorption capacity for lipophilic substances and a lower absorption capacity for polar substances [46]. DEHP has a higher molecular weight and longer alkyl chain than DnBP, DMP, BBP, and DEP, contributing to its stronger hydrophobicity.

The study confirms that PAEs are a type of endocrine-disrupting chemical that can pose risks to human health when ingested [9,47]. The grains of maize have the lowest PAEs content within the first 0–5 years of mulching, but higher levels of PAEs are found after ten years, which have certain health risks. Compared to maize leaves, the concentration of PAEs in stems is significantly lower. The height of the stem may dilute the concentration of hydrophobic pollutants and limit the transfer of pollutants from the leaves to the stem [14]. Cai [22] found that PAEs were absorbed by 20 rice varieties. The highest content of DnBP was in the leaves, followed by the roots, stems, and grains. Sun [48] discovered that the content of DnBP and DEHP in lettuce, strawberries, and carrot roots was significantly higher than in the leaves. Lu [24] found that PAEs are more prone to accumulate in ginseng leaves than in roots and stems. Ren [49] found that DnBP may be absorbed by the clover internally through adsorption onto the root epidermis and primarily accumulates in the roots. Li's [25] research indicated that PAEs are more likely to accumulate in Gaogengbai than Ziyoucai roots. Different plants exhibit diverse absorption and accumulation characteristics for different PAEs congeners [27,50].

In this study, the characteristics of the absorption, accumulation, and translocation of PAEs have been investigated in maize and cabbage, which are two common crops in local agriculture. The concentration of most PAEs congeners in maize is significantly higher than in cabbage (p < 0.05), indicating that maize has a higher ability to absorb or accumulate PAEs than cabbage. PAEs are mainly stored in the cell walls of roots, stems, and leaves, which is determined by the hydrophobicity of PAEs and the high lipid content of cell walls [43,51]. The lipid content in roots is generally considered a good indicator of hydrophobic compound absorption [49]. The PAE content in cabbage roots is significantly higher than that in maize roots, suggesting that cabbage roots have more lipids and can better adsorb PAEs from the soil, resulting in higher concentrations of organic pollutants in cabbage roots.

On the other hand, the uptake of organic pollutants by roots involves in the adsorption, precipitation, or absorption of soil pollutants [52]. In comparison, maize has well-developed and deep-rooted systems, which limits its ability to absorb PAEs, which are mainly distributed in the top soil. Our study found that the highest concentrations of DnBP and DEHP were present in the organs of cabbage and maize, consistent with previous research findings [44,53].

4.3. TF and BCF Characteristics of PAEs

Research has shown that crops can absorb and accumulate PAEs from the soil through their root systems [54]. Moreover, they also can absorb and accumulate PAEs from the air through their leaf stomata [55]. Consuming contaminated plants is the main pathway for human exposure to harmful compounds. Due to their widespread existence in the world and potential adverse effects on animals and humans, one of the significant risks associated with PAEs is their impact on human reproduction [56]. There is increasing attention on the accumulation, translocation, and hazards of PAEs in plants. To compare in-depth the differences in accumulation and translocation of five PAEs congeners in cabbage and maize organs under different mulching years, the bioconcentration factor (BCF) and translocation factor (TF) were calculated for maize and cabbage.

In addition, the absorption and translocation behavior of phthalate esters (PAEs) in vegetables is related to their physicochemical properties [50,54], such as the octanol/water partition coefficient (logKow) and the compound's logKow may be a determining factor in the plant absorption, translocation, or distribution processes [27]. Our study found that cabbage had a higher transfer factor (TF) for DnBP compared to DEHP (Table 1). It has been reported that organic compounds with logKow values between -1 and 5 are considered mobile under transpiration-driven processes. Therefore, DEHP, with a higher logKow value, was more prone to accumulate in plant roots [28].

Factor	Years	DMP	DEP	DnBP	BBP	DEHP	PAEs
RCF	СК	/	6.32 ± 0.24 a	$2.98\pm0.16\mathrm{b}$	0.00 ± 0.00	$6.22\pm0.58~\mathrm{d}$	$5.84\pm0.50~\mathrm{d}$
	10	/	$6.88\pm3.75~\mathrm{a}$	$0.42\pm0.08~{\rm c}$	/	$26.35\pm1.29\mathrm{b}$	$18.90\pm1.04~\mathrm{b}$
	15	/	$3.36\pm0.21~\mathrm{a}$	$2.98\pm0.07b$	0.00 ± 0.00	$31.45\pm0.98~\mathrm{a}$	$20.93\pm0.51~\mathrm{a}$
	30	6.26 ± 3.50	$4.29\pm1.67~\mathrm{a}$	$3.83\pm0.35~\mathrm{a}$	0.00 ± 0.00	$22.00\pm0.17~\mathrm{c}$	$16.86\pm0.43~\mathrm{c}$
	СК	/	$2.31\pm0.12~\mathrm{ab}$	$0.80\pm0.26~\mathrm{c}$	0.00 ± 0.00	$0.72\pm0.08~{\rm c}$	$0.71\pm0.08~\mathrm{d}$
LCF	10	/	$3.68\pm2.15~\mathrm{a}$	$1.38\pm0.15\mathrm{b}$	/	$7.24\pm0.78\mathrm{b}$	$5.56\pm0.51\mathrm{b}$
	15	/	$1.04\pm0.17~\mathrm{ab}$	1.35 ± 0.23 b	0.38 ± 0.11	10.92 ± 0.38 a	$7.36\pm0.31~\mathrm{c}$
	30	0.00 ± 0.00	$1.74\pm0.43~\mathrm{b}$	2.83 ± 0.24 a	0.31 ± 0.06	10.12 ± 0.30 a	$8.00\pm0.30~\mathrm{a}$
TF _{leaf}	CK	$0.77\pm0.15~\mathrm{a}$	$0.37\pm0.03~bc$	$0.27\pm0.08~\mathrm{b}$	/	0.12 ± 0.00	$0.12\pm0.00~d$
	10	$0.39\pm0.25\mathrm{b}$	$0.53\pm0.05~\mathrm{a}$	$3.34\pm0.73~\mathrm{a}$	/	0.28 ± 0.04	$0.30\pm0.04~\mathrm{c}$
	15	$0.35\pm0.05\mathrm{b}$	$0.31\pm0.06~{\rm c}$	$0.45\pm0.07~\mathrm{b}$	/	0.35 ± 0.01	$0.35\pm0.01~\mathrm{b}$
	30	$0.00\pm0.00~\mathrm{c}$	$0.42\pm0.06~b$	$0.74\pm0.09~\mathrm{b}$	/	0.46 ± 0.01	$0.47\pm0.01~\mathrm{a}$

Table 1. The bioconcentration factor (BCF) and translocation factor (TF) of phthalate esters in cabbage.

Note: different lowercase letters indicate significant differences between treatments (p < 0.05).

In this study, root concentration factor (RCF) values in maize under the mulching years of 0–20 were greater than the value of 1 (Table 2), indicating the accumulation of PAEs and their congeners in maize roots. The stem concentration factor (SCF) and leaf concentration factor (LCF) values of maize were higher than the grain concentration factor (GCF), suggesting that PAEs are more likely to accumulate in the stems and leaves of maize. Felizeter [57] investigated perfluorooctanoic and perfluorooctanoic acid uptake by lettuce. They noted that these chemicals can easily pass through (or bypass) the Casparian strip and accumulate in the leaf and grain-related vascular organs. It is speculated that a significant portion of vascular organs is present in the stems and leaves of maize, which explains the higher accumulation of PAEs in the plant.

Factors	Years	DMP	DEP	DnBP	BBP	DEHP	PAEs
RCF	СК	1.11 ± 0.58 a	0.00 ± 0.00	14.66 ± 1.61 a	0.23 ± 0.11	$2.97\pm0.47~\mathrm{b}$	3.25 ± 0.34 d
	5	1.52 ± 0.49 a	/	9.61 ± 1.58 b	0.00 ± 0.00	5.26 ± 0.09 a	5.58 ± 0.14 a
	10	1.96 ± 0.57 a	0.00 ± 0.00	$1.57\pm0.28~{ m c}$	1.39 ± 0.13	$6.25\pm0.18~\mathrm{c}$	$4.73\pm0.32\mathrm{b}$
	20	1.47 ± 0.59 a	4.37 ± 0.47	$0.96\pm0.10~{ m c}$	/	$4.91\pm0.22~\mathrm{b}$	$3.86\pm0.02~\mathrm{c}$
	CK	$0.91\pm0.03~\mathrm{a}$	1.15 ± 0.50	14.59 ± 0.04 a	0.70 ± 0.19	11.90 ± 0.73 a	10.96 ± 0.38 a
CCE	5	1.46 ± 0.50 a	/	$8.15\pm1.41~\mathrm{b}$	0.00 ± 0.00	$8.08\pm0.38\mathrm{b}$	$7.99\pm0.48\mathrm{b}$
SCF	10	$0.00\pm0.00~{ m b}$	1.72 ± 0.45	$0.95\pm0.14~{ m c}$	0.85 ± 0.41	$5.00\pm0.26~{ m c}$	$3.71\pm0.02~{ m c}$
	20	1.36 ± 0.37 a	1.43 ± 0.13	$0.62\pm0.03~{ m c}$	/	1.66 ± 0.09 a	$1.45 \pm 0.07 \text{ d}$
	CK	1.17 ± 0.21 a	5.25 ± 2.18	22.73 ± 0.31 a	2.64 ± 0.51	12.70 ± 0.99 a	12.27 ± 0.71 a
LCE	5	1.12 ± 0.54 a	/	$10.52\pm1.28\mathrm{b}$	19.43 ± 5.08	$6.83\pm0.18~\mathrm{b}$	$7.21\pm0.18\mathrm{b}$
LCF	10	$0.00\pm0.00~{ m b}$	3.67 ± 0.89	$1.34\pm0.13~{ m c}$	0.00 ± 0.00	$6.33\pm0.23\mathrm{bc}$	$4.77\pm0.30~{ m c}$
	20	1.52 ± 0.45 a	2.15 ± 0.14	$0.85\pm0.15~{ m c}$	/	$5.55\pm0.40~{ m c}$	$4.25\pm0.18~{ m c}$
	CK	1.23 ± 0.22	3.37 ± 1.11	19.46 ± 2.71 a	1.42 ± 0.26	$1.94\pm0.10~{ m c}$	$2.77\pm0.13~{ m c}$
CCE	5	1.51 ± 0.42 a	/	$6.83\pm0.39\mathrm{b}$	4.32 ± 0.93	1.22 ± 0.03 d	$1.69 \pm 0.05 \text{ d}$
GCF	10	3.11 ± 1.52 a	4.34 ± 1.50	$1.23\pm0.13~{ m c}$	5.62 ± 0.54	6.09 ± 0.14 a	4.62 ± 0.19 a
	20	3.41 ± 1.89 a	3.04 ± 0.52	$1.25\pm0.16~{ m c}$	/	$4.64\pm0.38~\mathrm{b}$	3.74 ± 0.14 b
TF _{stem}	CK	0.96 ± 0.43 a	/	1.00 ± 0.10 a	3.52 ± 1.69	4.05 ± 0.43 a	3.39 ± 0.25 a
	5	0.96 ± 0.15 a	0.25 ± 0.06	$0.85\pm0.10\mathrm{b}$	/	$1.54\pm0.05~{ m b}$	1.43 ± 0.05 b
	10	$0.00\pm0.00~{ m b}$	/	$0.61\pm0.03~{ m c}$	0.59 ± 0.23	$0.80\pm0.06~{ m c}$	$0.79\pm0.06~{ m c}$
	20	0.96 ± 0.13 a	0.33 ± 0.06	$0.65\pm0.04~{ m c}$	/	$0.34\pm0.02~\mathrm{d}$	$0.38 \pm 0.01 \text{ d}$
TF _{leaf}	CK	1.18 ± 0.36 a	/	1.56 ± 0.15 a	13.18 ± 5.89	4.31 ± 0.35 a	3.79 ± 0.19 a
	5	$0.71\pm0.12\mathrm{b}$	0.77 ± 0.08	$1.10\pm0.05\mathrm{b}$	/	$1.30\pm0.02~\mathrm{b}$	1.29 ± 0.02 b
	10	$0.00\pm0.00~{ m c}$	/	$0.86\pm0.11~{ m c}$	0.00 ± 0.00	$1.01\pm0.04~\mathrm{b}$	$1.01\pm0.03~{ m c}$
	20	1.06 ± 0.11 ab	0.50 ± 0.05	$0.88\pm0.07~{ m c}$	/	$1.13\pm0.05\mathrm{b}$	$1.10\pm0.04\mathrm{bc}$
TF _{grain}	CK	$1.24\pm0.37\mathrm{b}$	/	1.33 ± 0.16 a	6.83 ± 2.47	$0.66\pm0.09~\mathrm{b}$	$0.86\pm0.07\mathrm{b}$
	5	$1.00\pm0.09~\mathrm{b}$	0.71 ± 0.02	$0.72\pm0.09\mathrm{b}$	/	$1.29\pm0.02~{ m c}$	$0.30\pm0.02~{ m c}$
	10	1.53 ± 0.39 ab	/	$0.79\pm0.08\mathrm{b}$	4.05 ± 0.51	$0.97\pm0.03~\mathrm{a}$	$0.98\pm0.03~\mathrm{a}$
	20	2.20 ± 0.59 a	0.71 ± 0.18	1.30 ± 0.04 a	/	0.94 ± 0.04 a	0.97 ± 0.04 a
Note: different lowercase letters indicate significant differences between treatments ($n < 0.05$)							

Table 2. The bioconcentration factor (BCF) and translocation factor (TF) of phthalate esters in maize.

e: aimerent lowercase letters indicate significant differences between treatments (p < 0.05).

Due to the significant increase in root biomass of maize under plastic mulching [58], the BCFs (including RCF, LCF, SCF, and GCF) were lower in the mulching treatment compared to the non-mulching treatment. This could be attributed to the higher root biomass in the mulching treatment, which can also enhance the aboveground biomass of crops and dilute the concentration of PAEs. Our study calculated the maize plant BCF, which did not increase with the duration of mulching. Previous research has indicated that the migration of PAEs in crops is a complex process influenced by soil environmental effects, plant species, and chemical types [40]. Further research is needed to explore the exact translocation pathways of PAEs in crops.

The transfer factor (TF) of PAEs from maize roots to stems (TFstem) was more significant than 1 in the 0–5 years of mulching (Table 2), indicating a strong ability for PAEs to be transported from roots to stems under short mulching years. However, TFstem became less than 1 in the 10–20 years of mulching (Table 2) (p < 0.05), suggesting a gradual reduction in the transport capacity of PAEs from maize roots to stems with longer mulching years. The TF of PAEs from stems to leaves (TFleaf) was more significant than 1 in the 0–20 years of mulching (Table 2), indicating a consistently strong transport capacity of PAEs from stems to leaves (TFleaf) was more significant than 1 in the 0–20 years of mulching (Table 2), indicating a consistently strong transport capacity of PAEs from stems to leaves. This may be attributed to the well-developed vascular tissue in the stems and leaves of maize, as maize is a monocotyledonous plant with different structural characteristics compared to dicotyledonous plants like Chinese cabbage, which facilitates the transport from stems to leaves. The TF of PAEs from stems to grains (TFgrain) was significantly less than 1 in the 0–20 years of mulching (Table 2), but there was no significant difference with increasing mulching duration. This suggests a weaker transport capacity of PAEs from stems to grains in maize.

The root concentration factors (RCFs) in maize were significantly lower than those in cabbage (Tables 1 and 2), indicating that the ability of maize roots to absorb PAEs from the soil is lower than that of cabbage. This could be attributed to the higher lipid content in the roots of cabbage. Additionally, as a deep-rooted crop, the root system of maize mainly distributes in the deeper soil layers with lower PAEs content. The TF values of PAEs in maize were higher than those in cabbage, indicating a more vital transport capacity in maize. This may be due to more vascular tissue in maize plant parts, facilitating the translocation of PAEs between plant organs.

4.4. Correlation Analysis

The correlation analysis was conducted between six ratios in maize under different mulching durations and three ratios in cabbage with the physicochemical properties of PAEs compounds. The physicochemical properties of PAEs include logKow, molecular weight, solubility, and alkyl chain length, as shown in Table 3. LogKow is related to the hydrophobicity of compounds, ranging from 1.60 (DMP) to 8.71 (DEHP). The alkyl chain length represents the average of two alkyl chains, with DMP having the most petite chain length (1), followed by DEP (2), DIBP (4), DnBP (4), BBP (5.5), and DEHP (8). The logKow and alkyl chain length of the five PAEs increase while their solubility in water decreases, which is related to the increase in molecular weight.

Table 3. Physicochemical properties of the five PAEs, including partition coefficient of octanol/water (logKow), solubility, molecular mass (Weight), and alkyl chain length (Alkylchain) [25,50].

Analyte	Molecular Weight	Water Solubility	logKow	Alkyl Chain Length
DMP	194	4000	1.6	1
DEP	222	1080	2.47	2
DnBP	278.34	11.2	4.5	4
BBP	312.36	2.69	4.73	5.5
DEHP	390.526	0.00249	8.71	8

The correlation analysis results between the three factors in cabbage under mulching durations of 0–30 years and the characteristics of PAEs compounds are shown in Figure 6a.

LogKow is positively correlated with logRCF and negatively correlated with logTFleaf. These results indicate that PAEs with lower hydrophobicity have lower accumulation in plant roots but are more easily transported or accumulated in plant leaves. Li's [25] findings that the logKow values of PAEs were negatively correlated with logTFleaf and positively correlated with logRCF in cabbage and rapeseed, consistent with our results.



Figure 6. (a) Correlation analysis of cabbage three factors, and physicochemical property of PAEs (partition coefficient of octanol/water (logKow), solubility, molecular mass (Weight), and alkyl chain length (Alkyl chain). (b) Correlation analysis of maize six factors, and physicochemical property of PAEs (partition coefficient of octanol/water (logKow), solubility, molecular mass (Weight), and alkyl chain length (Alkyl chain). * indicates a significance level of p < 0.05; ** indicates a significance level of p < 0.05.

The correlation analysis results between the six factors in maize under mulching durations of 0–20 years and PAEs compounds are shown in Figure 6b. In maize with mulching 0–20 years, the logRCF, logSCF, logLCF, and logGCF values are all positively correlated with logKow. LogTFstem and LogTFleaf are positively correlated with logKow, while LogTFgrain is negatively correlated with logKow. These findings indicate that the hydrophobicity of the compounds significantly affects the absorption of pollutants by maize. PAEs with high hydrophobicity have a strong affinity for retention in maize's roots, stems, and leaves, while PAEs with low hydrophobicity are more easily transported to the grains.

5. Conclusions

This study reports novel findings regarding the absorption, accumulation, and translocation of PAEs in the soil-crop system under different mulching years. In this study, it was found that agricultural plastic film in farmland can release PAEs into the soil during degradation. Cabbage and maize, which are grown in the farmland, can absorb PAEs from the soil. Our research revealed differences in the accumulation and translocation patterns of PAEs in cabbage and maize plants. By calculating the BCF and TF, we observed a significant positive correlation between the increase in the duration of plastic film coverage and both the BCF and TF in cabbage. However, the correlation was not significant in maize. Our results reveal significant associations between the presence and distribution of PAEs in crops and the duration of mulching. Considering that the concentrations of PAEs in maize grains and cabbage leaves exceeded the relevant limits set by the Chinese Ministry of Health after mulching for more than ten years, further research is needed to assess the human health risks associated with PAE exposure through the dietary intake of maize and vegetables. Our observations suggest the need for better management of mulch recycling, as increasing mulching years result in higher detection of PAEs in maize grains and cabbage leaves. Overall, these novel findings provide fundamental information for developing national standards for controlling PAE pollution in agricultural environments.

Author Contributions: Conceptualization, H.Z. and X.N.; methodology, X.N.; validation, X.N. and K.M.; formal analysis, H.Z. and J.L.; resources, X.N., K.M., S.W. and H.Z.; data curation, H.Z. and J.L.; writing—original draft preparation, H.Z. and X.N.; writing—review and editing, H.Z., X.N., K.M. and T.M.; visualization, H.Z., X.N., K.M. and J.L.; supervision, H.Z., X.N., K.M. and S.W. All authors have read and agreed to the published version of the manuscript.

Funding: The research described in this paper was financially supported by the Ningxia Natural Science Foundation Project (2023AAC02020), National Natural Science Foundation of China (31960038) and the Key Project of Research and Development of Ningxia, China (2020BFG03006).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available upon request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

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