



Plastic film mulching increased the accumulation and human health risks of phthalate esters in wheat grains[☆]

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ABSTRACT

Plastic film mulching is a common practice to increase crop yield in dryland, while the wide use of plastic film has resulted in ubiquitous phthalate esters (PAEs) releasing into the soil. PAEs in soil could be taken up and accumulated by dietary intake of food crops such as wheat, thus imposing health risks to residents. In the present study, samples from a long-term location-fixed field experiment were examined to clarify the accumulation of PAEs in soil and wheat, and to assess the human health risks from PAEs via dietary intake of wheat grain under plastic film mulching cultivation in dryland. Results showed that concentrations of PAEs in grains from mulching plots ranged from 4.1 to 12.6 mg kg⁻¹, which were significantly higher than those in the control group. There was a positive correlation for the PAE concentrations between wheat grains and field soils. Concentrations of PAEs in the soil were in the range of 1.8–3.5 mg kg⁻¹ for the mulching treatment, and 0.9–2.7 mg kg⁻¹ for the control group. Di-n-butyl phthalate (DBP) and di-(2-ethylhexyl) phthalate (DEHP) were detected in all soil and grain samples, and DEHP was found to be the dominant PAE compound in grains. Based on DEHP concentrations in wheat grains, the values of carcinogenic risk for adults were higher than the recommended value 10⁻⁴. Results indicated that wheat grains from film mulching plots posed a considerable non-carcinogenic risk to residents, with children being the most sensitive resident group. Findings of this work call the attention to the potential pollution of grain crops growing in the plastic film mulching crop production systems.

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1. Introduction

Plastic film mulching has been used as an important water harvest and saving practice for efficient crop production in arid and semi-arid areas (Li et al., 2004). Plastic film mulching could help to alleviate the situation of low water supply in dryland by reducing water evaporation in soil, hence promoting crop growth and development (Kasirajan and Ngouajio, 2013). With the wide application of plastic film mulching in agricultural production, the amount of plastic film used increased significantly from 6,000 tons in 1982 to 1.2 million tons in 2011 (He et al., 2018). However, during the use and degradation of plastic film, pollutants, such as

phthalate esters (PAEs), could be continuously released into the soil, thus threatening the soil environment and food security for a long time (Luo et al., 2016).

PAEs are extensively-used plasticizers in plastic production to soften PVC, cellulose-based products, rubber and styrene (Steinmetz et al., 2016). Due to non-chemical bonding interactions with the polymeric products, PAEs can be easily leached out as hazardous contaminants into the environment (Kong et al., 2012; Chen et al., 2013). PAEs are reported to have endocrine disruptive effects on animals and humans, and some even cause potential mutagenicity, teratogenicity and carcinogenicity to human beings (Guo et al., 2012; Net et al., 2015). Six PAEs (namely, butyl benzyl phthalate (BBP), di-(2-ethylhexyl) phthalate (DEHP), dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DBP), and di-n-octyl phthalate (DOP)) were listed as environmental priority pollutants by the United States Environmental Protection Agency (USEPA, 2013). Hence, potential human exposure

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to PAEs in the environment or food chain has received great concerns in recent years.

PAEs have been widely detected in soils, vegetables, fruits, and grains (Mo et al., 2009; Fu and Du, 2011; Schecter et al., 2013; Cai et al., 2015; Wang et al., 2016; Lü et al., 2018). It was reported that in the Yangtze River Delta region, the total concentration of six kinds of phthalates was in the range of 0.17–9.37 mg kg⁻¹ in agricultural soil (Sun et al., 2016). In the Pearl River Delta region, the total amount of PAEs (Σ PAEs) in vegetable soil was as high as 46 mg kg⁻¹ (Cai et al., 2005). It is well accepted that phthalates in agricultural soil could be taken up and accumulated by plants. Nine types of greenhouse vegetable were reported to contain DEHP, and the range was 10.14–36.16 mg kg⁻¹ (Fu and Du, 2011). High concentrations of PAEs were also detected in cereals (such as rice and wheat) from China and the United States (Schecter et al., 2013; Lu et al., 2016).

As one of the main food crops, wheat is widely planted all over the world. In order to improve the yield of wheat, plastic film mulching cultivation has been widely used in the production of wheat in the arid and semi-arid areas (Li et al., 2004). However, plastic film mulching on the soil surface and the widespread residual film would cause the release of PAEs into the soil and even the accumulation in wheat grains, hence threatening the human health. Unfortunately, the potential PAE pollution in wheat grains caused by plastic film mulching hasn't been paid full attention. Most of the previous studies focus on the accumulation of PAEs in vegetables or rice from field soils (Lü et al., 2018), but few studies focus on wheat. The present reports on wheat focus on the toxicological effects of phthalate esters (Gao et al., 2016, 2017), and there is still a lack of systematic assessment of PAEs accumulation in wheat and soil under the field conditions.

Therefore, in the present study, a location-fixed field experiment with plastic film mulching was conducted in the Loess Plateau of China. The major objectives were aimed to investigate the distribution of PAEs in soil and wheat grains from plastic film mulching field, and to evaluate the human health risks of PAEs via dietary intake of wheat grains.

2. Materials and methods

2.1. Chemicals

Standards of DBP, DEHP, DnOP, BBP, DMP and DEP in hexane were purchased from Sigma Aldrich. All solvents, such as hexane and acetone, were of HPLC grade (Fisher Scientific). Anhydrous sodium sulfate, silica gel, and alumina oxide (from Sinopharm Chemical Reagent Co., Ltd.) were baked at 380 °C in a muffle furnace for 5 h before use. All phthalate solutions were stored in amber glass vials at -20 °C. Deionized water was prepared from Millipore Corp. system (18.2 M Ω cm).

2.2. Experimental design

The location-fixed field experiment was initiated from 2008 at Changwu County (35°12'N, 107°45'E, altitude 1200 m), Shaanxi Province, China. The annual average temperature from 1957 to 2017 was 9.1 °C, and the mean precipitation was 579 mm. The soil in Changwu is classified as a Cumuli-Ustic Isohumosols (USDA system), and the basic soil physicochemical properties in 0–40 cm layer were listed in Table S1. The winter wheat used is a local cultivar "Changwu521".

The experiment included two treatments of plastic film mulching pattern (PM) and control, which were arranged in a randomized complete block design. All treatments were replicated four times with the plot size of 22 × 6 m². For the control, winter

wheat was planted in a traditional flat planting, and the soil surface was kept bare during the whole wheat growing season. While for PM, the soil was prepared in a ridge-furrow pattern at seeding, with the ridge mulched with plastic film (with a thickness of 8 μ m) and furrow bare for seeding. The plastic film was kept to mulch the soil surface during the winter wheat growing, and it was removed and replaced with a new plastic film at the next wheat sowing. For all treatments, winter wheat was sown during the date of Sept.20 - Oct.15, and harvested during Jun.20–30 of the next year. The wheat was harvested with a combine harvester, and straw was crushed and returned to the field. No additional irrigation was supplied, and fertilizer application rates were 150 kg N ha⁻¹ and 105 kg P₂O₅ ha⁻¹, same for both treatments.

2.3. Sample collection

Soil samples were collected at the same time of wheat harvest in the year 2013 (sown in Sept. 2012), 2015 (sown in Oct. 2012) and 2017 (sown in Sept. 2016). In each plot, five cores of 0–20 cm soil were sampled from different sites and completely bulked to form a composite sample. For the physicochemical property analysis, soil was air-dried, ground, sieved through a 2 mm sieve and determined according to standard procedures (Bao, 2007). As for PAE analysis, the soil was freeze-dried and ground to a fine powder (0.25 mm) using a stainless-steel grinder, and stored at -20 °C before analysis.

Plant samples were also collected at the harvest stage. For each sample, 100 ears from each plot were randomly selected. After being threshed, wheat grains were rinsed with deionized water, freeze-dried then ground by a stainless-steel grinder. The fine-ground plant samples were stored at -20 °C before analysis.

2.4. Analysis of PAEs

The extraction and cleanup of soil and plant samples were performed based on the previous report (Xu et al., 2018). Briefly, a 0.5 g aliquot of soil sample or grain sample was placed in a 50 mL glass centrifuge tube, then benzyl benzoate was added as a recovery surrogate, followed by extraction with a 20 mL mixture of acetone and hexane (1:1 v/v). After mixing in a vortex for 1 min, the mixture was extracted in an ultrasonic bath for 30 min, then centrifuged at 3500 rpm for 30 min. The supernatant was transferred to a 50 mL glass bottle, and the residue was extracted once more with 20 mL fresh mixture of acetone and hexane (1:1 v/v). All of the obtained supernatants were reduced to about 2 mL using rotary evaporator, added 5 mL hexane and then rotary evaporated to 1 mL again. The above concentrates were passed through a glass chromatographic column (anhydrous sodium sulfate: alumina: neutral silica gel = 1:3:6 by mass). The received eluent was reduced to 1 mL using a nitrogen blowing apparatus prior to analysis.

PAEs in the obtained eluent were measured using gas chromatography-mass spectrometry (ThermoFisher TRACE1310-ISQLT) coupled with a 30 m × 0.25 mm × 0.25 μ m TG-5 capillary column (Thermo). The carrier gas was high purity helium maintained at the flow rate of 1.2 mL min⁻¹. The temperature settings were as follows: 50 °C maintained for 1 min, increased to 120 °C at 15 °C min⁻¹, hold for 1 min, and finally raised to 280 °C at 8 °C min⁻¹ (hold for 3 min). Each extract (1 μ L) was injected into the splitless mode. The injector temperature was set to 250 °C.

Phthalate quantitation was performed according to five-point calibration curve, which were obtained by diluting 10 μ g mL⁻¹ mixed stock standard solution to concentrations of 0, 0.1, 0.3, 0.5, 1.0, 2.0 μ g mL⁻¹. All the stock and working solutions were prepared in hexane. Concentration in soil and wheat grains were normalized to dry weight.

It should be mentioned that no plastic instruments were used

throughout the test. All the glass containers were carefully soaked in nitric acid solution (20%), then washed with deionized water followed by acetone for several times, then baked at 120 °C for 12 h and washed with acetone and hexane before use. The procedural and spiked blanks were included for every ten samples. The surrogate recoveries of PAEs were ranged from 89.3% to 117.1%. The detection limits of PAEs using this method were 2.5 µg L⁻¹.

2.5. Risk assessment model

Non-carcinogenic and carcinogenic risks of toxic phthalates were calculated using Eqs. (1)–(3) (USEPA, 2013). The non-carcinogenic risk (NCR_i) of each toxic phthalate exposed to local residents from the city or the countryside of different ages and genders was calculated according to Eq. (1). It indicates that the amount of PAEs exposed to the human body has a potential risk if NCR_i is greater than 1.0. Otherwise the risk is within an acceptable range. NCR was the sum of the NCR_i of all PAEs in each treatment, which was calculated by Eq. (2). Carcinogenic risk (CR) to the population through food intake was calculated by Eq. (3). The daily intake of wheat grains and the average body weight of 16 groups of residents is shown in Table S2, which is based on Chinese national health and nutrition survey (Zhai and Yang, 2006).

$$NCR_i = \frac{C_n \times D_n \times EF_r \times ED_{tot}}{RfD \times BW \times AT_n} \quad (1)$$

$$NCR = \sum_i^n NCR_i \quad (2)$$

$$CR = \frac{C_n \times D_n \times CPS_0 \times EF_r \times ED_{tot} \times 10^{-3}}{BW \times AT_n} \quad (3)$$

Where:

NCR_i = the NCR of individual phthalate compound, and *i* could be DBP, DEHP, BBP or DEP.

NCR = the sum of the NCR_i for all PAEs;

CR = the carcinogenic risk;

C_n = concentration of PAEs in grains (mg kg⁻¹); D_n = daily intake of wheat grains (g d⁻¹);

EF_r = exposure frequency (365 d year⁻¹); ED_{tot} = exposure duration (year), the values for residents in the ages of 4–10, 11–17, 18–60, and 61–70 were 7, 7, 43, and 10 years, respectively;

AT_n = average time of exposure to PAEs (ED_{tot} × 365 d year⁻¹ for non-carcinogenic risk; 25,550 d for carcinogenic risk)

BW = average body weight (kg);

RfD = reference dose (µg kg⁻¹ d⁻¹). The reference doses for DBP, DEHP, BBP and DEP are 100, 20, 200, and 800 µg kg⁻¹ body weight d⁻¹ (USEPA, 1987);

CPS₀ = carcinogenic potency slope (USEPA, 2009), and CPS₀ of DEHP is 0.014 per (µg g⁻¹ d⁻¹) (USEPA, 2013).

2.6. Statistical analysis

SPSS 19.0 (SPSS Inc., USA) was used to test the homogeneity of variance, and then the multivariate statistical analysis program was run to compare the significance of differences between the two cultivation patterns (*t*-test and *P* < 0.05).

3. Results and discussion

3.1. Soil PAEs

The concentrations of soil ΣPAEs in different treatments were presented in Fig. 1. Soil ΣPAEs in PM (1.8–3.5 mg kg⁻¹) were higher than those in control (0.9–2.7 mg kg⁻¹) in the three years. The levels of soil ΣPAEs in this study were slightly lower than those of soil samples from East China, which was reported with the maximum of 18.8 mg kg⁻¹ (Li et al., 2016) or 7.1 mg kg⁻¹ (Hu et al., 2003). However, they were significantly higher than those in Denmark (0.014–2.5 mg kg⁻¹) (Vikelsøe et al., 2002), Scotland (0.025–1.60 mg kg⁻¹) (Rhind et al., 2013), Serbia (0.19–2.12 mg kg⁻¹) (Škrbića et al., 2016), or the UK (0.042–0.099 mg kg⁻¹) (Gibson et al., 2005). Results in the present study illustrated that the plastic film mulching could induce the accumulation of PAEs in the soil to some extent, but the level of soil PAEs was lower than the soil environmental quality limits (10 mg kg⁻¹) for cultivated land soil (GB15618-1995) (Ministry of Environmental Protection and Ministry of Land and Resources of China, 2014).

In the six tested PAEs, only DBP and DEHP were obviously detected in soil samples (Fig. 1). For all soil samples, concentrations of DEHP (with the range of 0.46–2.30 mg kg⁻¹) were higher than those of DBP (0.45–1.41 mg kg⁻¹). In this study, DEHP and DBP were the dominant phthalates in all soil and grain samples, which was consistent with the previous studies (Zeng et al., 2008; Lü et al., 2018). These results may be attributed to the properties of PAE monomers. It was reported that the migration and transportation of phthalates in the soil were related to their physical and chemical properties (Staples et al., 1997). PAE compounds with short chains, such as DMP and DEP, have shorter biodegradation half-lives in soil due to their higher water solubility and lower octanol-water partition coefficient. In contrast, long-chain PAEs species with lower water solubility, such as DEHP, are easily adsorbed by soil and difficult to biodegrade (Staples et al., 1997).

No significant differences of the soil DEHP or DBP were observed among different years for the same treatment (Fig. 1), and soil PAEs did not increase with the elongation of plastic film mulching duration. The content of PAEs in the soil was affected by both the release from plastic film and the natural removal (from volatilization, leaching, biodegradation and plant uptake) (Staples et al., 1997). The release of PAEs could be influenced by the temperature, the film thickness and the amount of residual film debris (Lü et al., 2018). As for the removal of PAEs, temperature, microbial

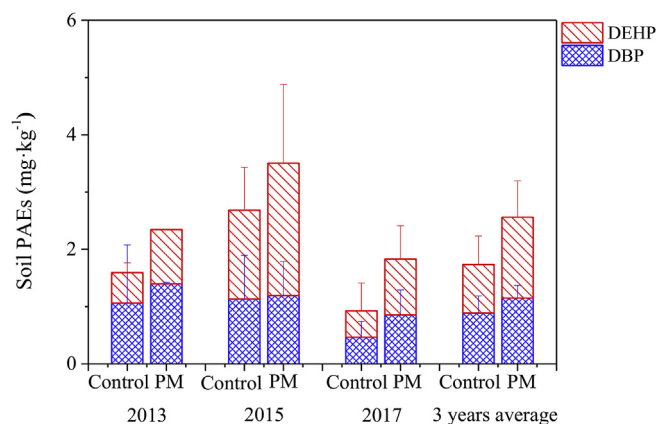


Fig. 1. Effects of plastic film mulching on concentrations of PAEs in soil in the three experimental years. PM represents the plastic film mulching treatment.

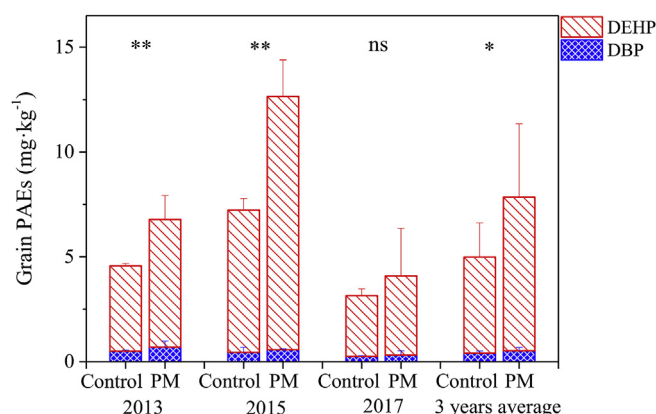


Fig. 2. Effects of plastic film mulching on concentrations of PAEs in winter wheat grain in the three experimental years. One asterisk "*" ($P < 0.05$) or two asterisks "**" ($P < 0.01$) above a pair of columns represent the significant difference between control and plastic film mulching (PM) treatments in the same year or the 3 years average.

activity and plants may play an important role on the process (Staples et al., 1997). In this study, the amount of residual film was low due to the artificial removal every year, hence the content of PAEs in soil may be the result of a combination of factors from temperature, microorganisms, and plants.

3.2. Grain PAEs

Compared with the control, plastic film mulching significantly increased the total PAEs concentration in grains (Fig. 2). For PM, concentrations of the sum of detected PAEs (Σ PAEs) in wheat grains ranged from 4.1 to 12.7 mg kg^{-1} with an average of 7.8 mg kg^{-1} in the three years, which were 1.3–1.7 times of those in control. The levels of Σ PAEs in grains from mulching plots in this study were higher than those in the United States, as reported by Schecter et al. (2013).

For all grain samples, DEHP was the dominant phthalate (89%–

96%), followed by DBP, while concentrations of four other PAEs species were below the detection limits (Fig. 2). Concentrations of grain DEHP in PM were in the range of 3.8–12.1 mg kg^{-1} , which is significantly higher than those in control. As observed for PM, concentrations of DEHP in grains varied considerably over different years, with the highest point in 2015 (12.1 mg kg^{-1}) and the lowest in 2017 (3.8 mg kg^{-1}). High concentrations of DEHP (11.2–34.0 mg kg^{-1}) were also detected in vegetables in the previous study (Fu and Du, 2011). Moreover, the detection frequency of DEHP was the highest in the study on PAEs exposure from foods (like fruits, grains, and pork) in New York (Schecter et al., 2013). It indicated that DEHP was widely present in the food chain, and the exposure to DEHP needed a more representative survey.

3.3. Factors affecting concentrations of PAEs in wheat grains

Results of the present study showed that concentrations of PAEs in wheat grains varied significantly among different years. Many factors, including 1) dilution effect due to yield increase, 2) concentrations of PAEs in the soil and 3) climatic factors (such as temperature), may lead to the above variation. The dilution effect due to yield increase was excluded, because of no significant correlation between grain yields and the PAE concentrations in wheat grains (Fig. 3a). For the other two factors, the corresponding analyses are as follows.

Results represented a significant positive correlation for the PAE congener concentrations between field soils and wheat grains (Fig. 3b), indicating that the accumulation of PAEs in wheat may be mainly from root uptake from the soil. For the correlation between PAEs in field soils and in plants, there were no consistent results in previous studies. The concentrations of PAEs in wastewater irrigated wheat and maize were found to have a high correlation with those in soils (Tan et al., 2016), while unclear relationships were observed for the concentrations of PAEs in vegetables and soils from plastic film greenhouses (Wang et al., 2015; Chen et al., 2017). The inconsistency from different reports indicates that the accumulation of PAEs in plants may be affected by the types of plants

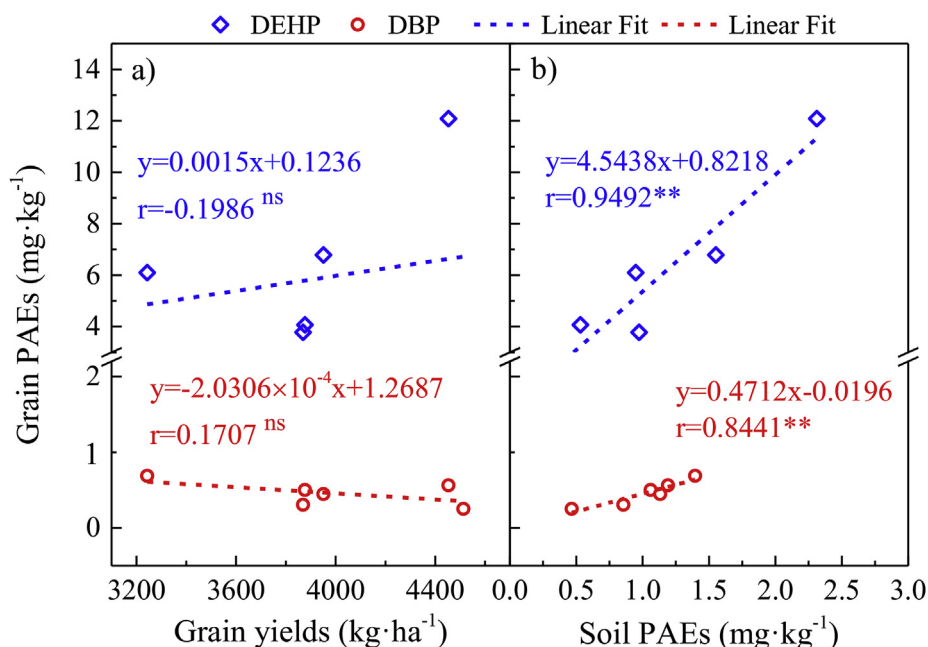


Fig. 3. Correlations of PAE congener concentrations in wheat grains with grain yields (a), and PAE congener storages in soils (b). Circles and rhombuses denote DEHP and DBP respectively. Two asterisks (**) indicate statistically significant ($P < 0.01$), and "ns" indicates no significant difference.

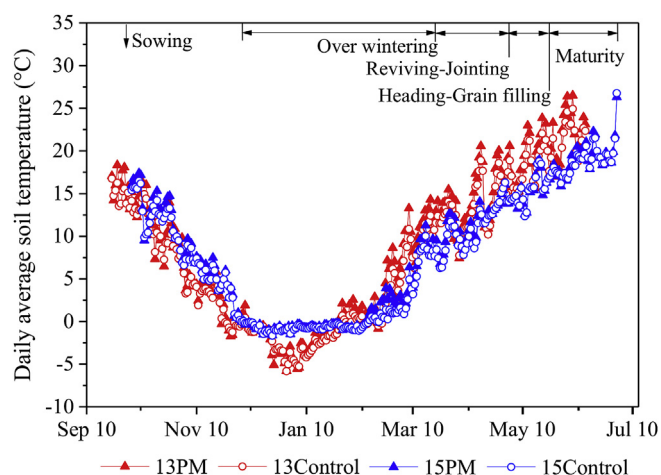


Fig. 4. Distribution of 0–5 cm soil temperature in winter wheat growing seasons of 2012–2013 and 2014–2015. 13PM and 13 Control represent the plastic film mulching (PM) and control treatments in the experimental year of 2012–2013; 15PM and 15 Control represent those for the experimental year of 2014–2015.

and the ways of using plastic films, such as used as the greenhouse shelter to cover all the plants or just as a soil surface cover.

The climate factor, especially the temperature, was another factor affecting the accumulation of PAEs in wheat grains. Therefore, changes of soil temperature were monitored during winter wheat growing seasons of 2012–2013 and 2014–2015 in the field experiment (due to the malfunction of equipment, the data of 2016–2017 is missing). It showed that soil temperatures from sowing to the end of January (from the seeding to tillering stage) were higher in the crop season 2014–2015 than those in 2012–2013, while the result was the opposite after March of following year (Fig. 4). The results indicated that the higher temperature during the seedling and tillering stages may contribute to the higher uptake of PAEs by wheat, and then result in the higher concentration of PAEs of wheat grain collected in 2015. If this hypothesis is established, one of the prerequisites is that the uptake of PAEs by wheat is mainly in seedling and tillering stages but not in other stages. The above inference was evidenced by the previous study using a pot experiment (Dong, 2018), which showed that the concentration of DBP or DEHP in wheat decreased with the growth of wheat. In fact, the temperature may affect many aspects, such as the release of PAEs from plastic film into soil, the degradation of PAEs by soil microorganisms, and the uptake of PAEs by plants (Lü et al., 2018). However, the influence of temperature on PAEs concentrations in the soil-wheat system needs to be further studied.

3.4. Human health risks

PAEs in wheat grains could pose health risks to human beings through the food chain. Non-carcinogenic risks of DBP and DEHP to different groups of residents via dietary intake of wheat grains were shown in Table 1. Results showed that the main contribution of PAEs to non-carcinogenic risk came from DEHP, and wheat grains from plastic film mulching plots exhibited higher risks than those from the plots in control. The non-carcinogenic risk of DEHP (ranging from 0.458 to 1.518) was significantly higher than that of DBP (in the range of 0.008–0.022).

NCR (non-carcinogenic risk) represents the cumulative effect of PAEs via dietary intake (Fig. 5). For the control, the PAEs evaluated in the wheat grains presented a safe NCR (<1.0) for all residents in both the city and the countryside. However, for PM, NCR of PAEs in wheat grains exceeded 1.0 for male residents in all ages and females

Table 1

Non-carcinogenic risks (NCR_i) of DBP and DEHP to different groups of residents via dietary intake of wheat grains with (PM) and without plastic film mulching (Control).

Year	Treatment	Age	City		Countryside			
			Male	Female	Male	Female		
DBP	Control	4–10	0.012	0.012	0.016	0.017		
		11–17	0.010	0.008	0.013	0.012		
		18–60	0.009	0.008	0.012	0.010		
		61–70	0.008	0.008	0.011	0.010		
	PM	4–10	0.016	0.015	0.020	0.022		
		11–17	0.012	0.011	0.016	0.016		
		18–60	0.011	0.010	0.015	0.014		
		61–70	0.011	0.011	0.014	0.013		
		DEHP	Control	4–10	0.697	0.683	0.898	0.951
				11–17	0.548	0.474	0.725	0.704
18–60	0.492			0.458	0.659	0.600		
61–70	0.479			0.469	0.638	0.572		
PM	4–10		1.114	1.092	1.434	1.518		
	11–17		0.875	0.758	1.158	1.125		
	18–60	0.786	0.731	1.052	0.959			
	61–70	0.766	0.749	1.020	0.914			

aged 4–10 in the countryside. People living in the countryside had a higher hazard risk than those living in the cities (as shown in Fig. 5). It was also shown that the risk for children was significantly higher than that for other groups, which may be due to the lower body weight. For children, the development of organs and the nervous system is still not mature, so the damage caused by harmful substances may be more profound. In this regard, the potential risks for the children exposed to PAEs should be paid more attention.

CR was used to assess the carcinogenic risk to residents exposed to target phthalate in wheat grains. The recommended acceptable or inconsequential risk level for the population developed by USEPA is 1×10^{-6} . However, additional lifetime cancer risk equals 1×10^{-4} or higher is considered serious (USEPA, 1996). In the two detected PAE compounds, only DEHP has potential carcinogenicity. Based on concentrations of DEHP in wheat grains, carcinogenic risks for different groups of population were calculated and present in Table 2. The values of CR for all population groups fell in the range of 10^{-5} – 10^{-4} . The average values of CR based on DEHP were higher for males than those for females, which was in accordance with dietary intake of wheat grains. As for the population age, it can be observed that adults (in the age of 18–60) had the highest risk, followed by children (in the age of 4–10), and adolescents (11–17) suffered the lowest risk for both males and females.

Due to the fact that human beings could be at the risk of PAEs via inhalation (Miao et al., 2017) and dermal contact exposure from the environment (Lu et al., 2016), and the ingestion exposure from other foods (Wang et al., 2016), the risk value in the present study might underestimate the actual conditions. Therefore, it should be realized that although plastic film mulching could increase food production in the short term (Steinmetz et al., 2016), the consequential PAEs pollution and food safety problems must not be neglected.

4. Conclusion

In the present study, the effects of plastic film mulching on PAEs in soil and wheat grain were examined by the analysis of samples collected over three years from a long-term location-fixed field experiment. Plastic film mulching significantly increased the concentrations of PAEs in wheat grains, which was in the range of 4.1 – 12.6 mg kg^{-1} . Higher PAEs in grains may be attributed to higher PAEs in soil and higher temperature in the seeding and tillering stages. DEHP and DBP were detected in all soil and grain samples,

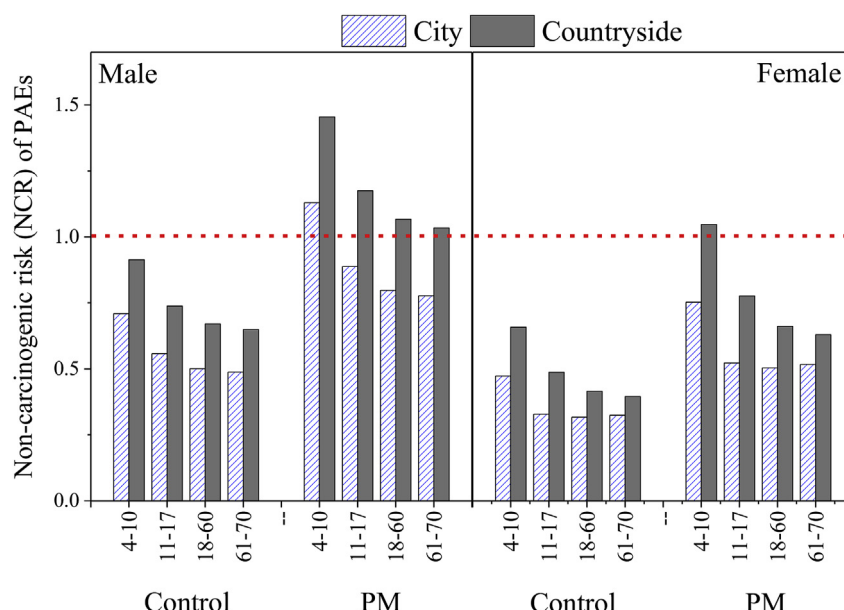


Fig. 5. Non-carcinogenic risk (NCR) to different groups of residents via dietary intake of wheat grains based on the average of Σ PAEs in three years. PM represents the plastic film mulching treatment.

Table 2
Carcinogenic risk (CR) of DEHP to different groups of residents via dietary intake of wheat grains with (PM) and without plastic film mulching (Control).

Treatment	Ages	City		Countryside	
		Male	Female	Male	Female
Control	4–10	1.95E-05	1.91E-05	2.51E-05	2.66E-05
	11–17	1.53E-05	1.33E-05	2.03E-05	1.97E-05
	18–60	8.47E-05	7.87E-05	1.13E-04	1.03E-04
	61–70	1.92E-05	1.88E-05	2.55E-05	2.29E-05
PM	4–10	3.12E-05	3.06E-05	4.02E-05	4.25E-05
	11–17	2.45E-05	2.12E-05	3.24E-05	3.15E-05
	18–60	1.35E-04	1.26E-04	1.81E-04	1.65E-04
	61–70	3.06E-05	3.00E-05	4.08E-05	3.65E-05

and DEHP was the dominant phthalate compound. The present study indicates that grains from the plastic film mulching plots had the unignorable non-carcinogenic hazardous risk and carcinogenic risk to residents. Findings of this work provide information for the protection of cultivated land soil and for the safe production of grain crops growing in the plastic film mulching crop production systems.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2019.03.064>.

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