

Empirical estimation of pollution load and contamination levels of phthalate esters in agricultural soils from plastic film mulching in China

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Abstract Pollution load and contamination levels of phthalate esters (PAEs) in agricultural soils throughout China were studied in this work. The usage amount and residual rates of plastic film were the main factors explaining the variation among regions and leading to higher pollution load and contamination levels in agricultural big provinces. However, higher pollution loads and contamination levels frequently occurred under non-recycling than recycling scenarios during calculation. Extremely high loads (more than 10 kg/ha/year) of PAEs were estimated in five areas including Beijing city, Tibet, Liaoning Province, Jilin Province and Fujian Province and the high contamination levels in agricultural soil were presented in these places with more than 4.0 mg/kg under non-recycling scenarios. The predicted concentrations of PAEs in soils exceed the target value for soils from Netherlands (Σ PAEs = 0.1 mg/kg), indicating very high contamination of most Chinese agricultural soils. Significant differences in estimation results after plastic film utilization suggest that decreasing plastic film residue after application is an effective measure to control PAE pollution in soils. However, the comparison between contamination levels of

PAEs estimated by the model and the previous detections of PAEs pollution levels in agricultural soils showed that there were presented wide range of PAE sources indicated to agricultural soils.

Keywords Phthalate esters · Plastic film mulching · Pollution load · Contamination levels · Empirical estimation · Scenario

Introduction

Phthalate esters (phthalic acid esters, PAEs) are common plasticizers used to increase the flexibility, extensibility and ease of processing (workability) of polyvinyl chloride (PVC), with a constituent up to 50 % of the total weight of PVC plastics (van Wezel et al. 2000). PAEs are not irreversibly bound to the polymer matrix, but present in the PVC as a freely mobile and leachable phase, resulting in migrating from the plastic to the external environment under certain conditions (Balafas et al. 1999; Gómez-Hens and Aguilar-Caballeros 2003; Colombani et al. 2009). The yearly production of PVC is approximately 20 million tons, and it was estimated that the PVC waste amounts were up to 5.4 million tons in 2010 and a 40 % rise of that waste is likely to occur in 2020 (Teil et al. 2006). Therefore, the environmental contamination levels will be enhanced because of the worldwide utilization of PAEs in plastic industry. At the present time, ubiquitous and serious contamination of PAEs in environmental matrices such as soil, water and air, has been reported in numerous studies (Mayer et al. 1972; Staples et al. 1997; Peijnenburg and Struijs 2006; Teil et al. 2006; Zeng et al. 2008).

After entering the environment, PAEs are redistributed among solid, aqueous and gas phases. Sorption,

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biodegradation, valorization and deposition may occur during PAEs' presentation processes. However, sustained release of PAEs from the plastic materials made the frequency detections of these compounds in environmental matrices. Some PAEs and their metabolites have been found to exhibit reproductive and developmental toxicities in laboratory animals and are regarded as a type of endocrine disruptor in environmental pollutants (Gray et al. 2000; Chen and Sung 2004; Matsumoto et al. 2008). Regulations have been made to control the widespread distribution of PAEs in the environment, especially of materials that have direct contacted with humans (Balafas et al. 1999; Amato et al. 2001). However, little consideration has been given to the plastic films used in agricultural production systems, despite the increasing use of these materials in crop cultivation.

In China, more than 1 million tons of plastic films are used each year in agricultural production to promote or protect crop growth (Department of rural social and economic investigation 2009). This indicates that relatively large amounts of plasticizers such as PAEs may be released into the environment from plastic films used for mulching (Gómez-Hens and Aguilar-Caballeros 2003; Nørbygaard and Berg 2004; Navarro et al. 2010). Moreover, the plastic films used in agriculture are not recycled efficiently and some are allowed to remain in fields as fragments (up to 317.1 kg/ha/year in Chinese vegetable fields). These residual mulching plastic films may persist in the field for long periods of time (up to 200–400 years) and continue to release PAEs into the soils (Wu 1994; Wang 1998; Xu et al. 2005).

Previous studies have shown that Chinese agricultural soils contain high levels of PAEs measured in magnitude of mg/kg (Hu et al. 2003; Ma et al. 2003; Zeng et al. 2008; Chen et al. 2011). However, there have been few studies on the relationship between mulching with plastic film and PAE pollution levels in agricultural soils. The present study was therefore conducted to examine this relationship based on model calculation to estimate the pollution load and contamination levels of phthalate esters in soils on a national scale by empirical calculation. The calculations were based on the usage amounts of mulching plastic film and the residual rates of the films after their application. The aim was to identify effective control measure for PAE pollution by comparison between two plastic film management scenarios, recycling versus non-recycling.

Materials and methods

Model hypothesis

Phthalate esters released from plastic film into soils are affected by numerous factors such as the release rate from

PVC to soil, the degradation or dissipation rate in the soil and migration from soil to other environmental media. However, entrance and dissipation may occur simultaneously and their balance is determined by different factors such as climate, soil conditions and physicochemical properties of the compounds. It is difficult to develop algorithms to evaluate these environmental processes because of the lack of experimental data from laboratory and field. Thus, some hypothesis as below was assumed to fit the model calculation.

- No other sources of PAEs are present in the areas.
- Mulching plastic films lying on the soils are well-distributed.
- All PAEs will be rapidly released into soils from residual films.
- No degradation or dissipation of PAEs occurs in the soils.
- PAEs in soils do not transfer to surface waters, groundwater, air or elsewhere.
- PAEs released from residual films are well distributed in the topsoil (0–20 cm depth).

Model description

The utilization of plastic film mulching introduced the residual film pollution into soil environment, leading to the contamination of PAEs. Based on this principle, the residual film pollution is calculated by the amount of plastic film used and its residual rate, and the pollution load of the PAEs can be estimated by residual amount of plastic films and the proportion of PAEs in the films. Finally, pollution loads and contamination levels in the agricultural land mulched by plastic film can be calculated by the pollution load of the PAEs and soil area or soil weight. The model algorithms are detailed as follows:

$$\text{RFP} = F_M \times F_r, \quad (1)$$

where RFP is the residual film pollution, measured in tons; F_M the amount of mulching plastic film used, measured in tons and F_r is the residual rate of mulching plastic film in the soils after its application, measured in %, which is defined as percentage residual amount of the total amount of mulching plastic film used; the residual amount is calculated by the net increase between the total residual amount of plastic films in soils after crop harvest and the residual amount of plastic film before mulching.

$$\text{PAE}_{\text{total}} = \text{RFP} \times P_c \times \text{PAE}_c, \quad (2)$$

where $\text{PAE}_{\text{total}}$ is the total amount of PAEs released into agricultural land mulched by plastic film, measured in tons; P_c the content of plasticizers in PVC products by weight,

measured in % and PAE_c is the proportion of PAEs used as plasticizers in plastic film production, measured in %.

$$PAE_{load} = \frac{PAE_{total}}{A}, \quad (3)$$

where PAE_{load} is the pollution load of PAEs in agricultural land mulched by plastic film, measured in kg/ha/year and A is the area of agricultural land mulched with plastic film, measured in ha.

$$PAE_{soil} = \frac{PAE_{total} \times 10^9}{SW} \quad (4)$$

$$SW = A \times D \times \rho, \quad (5)$$

where PAE_{soil} is the contamination levels of PAEs in topsoil in the agricultural land mulched with plastic film, measured in mg/kg; 10^9 the unit conversion factor between t and mg; SW the weight of topsoil in the agricultural land mulched with plastic film, measured in kg; A the area of agricultural land mulched with plastic film, measured in m^2 ; D the depth of agricultural land in which PAEs are present, measured in m and ρ is the bulk density of the soil, measured in kg/m^3 .

Determination of model parameters

According to the parameter descriptions, F_M and A can be obtained directly from the statistical yearbook. The others are available from references and used for calculation. The processes used for determining parameter values are described below.

F_M and A were obtained from the Chinese Rural Statistical Yearbook 2009 (Department of rural social and economic investigation 2009), and the data were recorded separately for different provinces or cities (Table 1; Fig. 1).

It is difficult to obtain an accurate residual rate of mulching plastic film for each province or city as it is affected by many factors such as cropping system, climate, cultivation practices, soil type and plastic film type. In different regions, F_r was a variable and the detailed values in estimation were determined according to the China Pollution Source Census (discussed in the results).

The amount of plasticizer in PVC formulations depends on the required properties and can vary from 15 to 60 wt% as a function of the final application. In general, formulations with around 35–40 % plasticizer are the most common in PVC production (Gómez-Hens and Aguilar-Caballeros 2003; Nørbygaard and Berg 2004; Navarro et al. 2010). In the present study, P_c was assumed to be 35 % for the model.

There are no data available on the amounts of PAEs used as plasticizers during plastic film production in China. It has been reported that 88 % plasticizer in consumption is

PAEs worldwide and about 70 % in the USA (Tao and Liang 2008; Stuart et al. 2010). The value of 70 % for PAE_c was therefore used for calculation for conservation in the present study.

D is the depth of topsoil in which the PAEs are present. D was taken as 0.2 m for calculation.

The value of ρ can also vary among different agricultural regions but for ease of comparison $1,500 \text{ kg/m}^3$ was used in the present study.

Results

Determining the F_r in agricultural land in China

Most plastic film enters the soils after mulching because it is difficult and time consuming to recycle, resulting in a large amount of plastic film pollution on agricultural land that has been mulched with plastic film (Wu 1994; Wang 1998). According to China Pollution Source Census, the Chinese agricultural lands mulched by plastic films can be divided into six growing regions with two management scenarios (recycling and non-recycling). The residue rates from different fields in these regions were calculated by fixed position investigations (total 432 positions in whole countries) conducted over 1 year, based on the examination of 5 pits (each 2 m^2 in area and 20 cm deep) in each mulching area with an area of about 667 m^2 (the selected pits were positioned in a quincunx geometric pattern in each survey area). The results showed that recycling management (recycling or non-recycling) was the most important factor affecting plastic film pollution in mulching areas (Table 1; Fig. 1). It is difficult in practice to recycle plastic film after it has been used in the field, especially in large productions areas such as cotton fields because the film is thin, flexible and readily broken up into small fragments during cultivation. As a result, ubiquitous plastic film pollution has been occurring in these agricultural lands mulched with plastic film (Du et al. 2005; Ma et al. 2008). In addition, the climate and topography of different regions also affect the residue rates to a great extent, leading to high variation in pollution under the same film management practice (Table 1).

Pollution load of PAEs across China

The amounts of PAEs released based on plastic film pollution were expected to be dependent on the amount of mulching plastic film used and residual rates from different provinces or cities. Figure 2 presents the pollution load of PAEs released from plastic film across China. Under the non-recycling scenario, five areas (Beijing City, Tibet, Liaoning Province, Jilin Province and Fujian Province) released PAEs

Table 1 Data information for model calculation

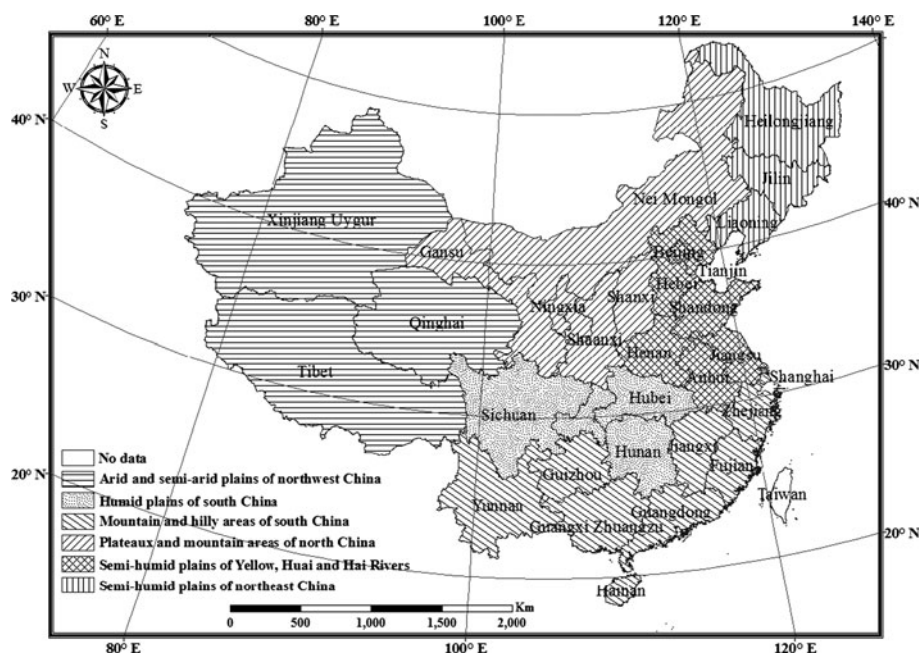
Region	Provinces or cities	Total plastic film load (t/year)	Residual rates (%) ^a in non-recycling scenario	Residual rates (%) ^a in recycling scenario	Plastic film mulched land area (ha)
Plateaux and mountain areas of north China	Inner Mongolia Autonomous Region	39,070.0	29.7	4.9	736,174
	Shaanxi Province	18,981.0	29.7	4.9	439,338
	Gansu Province	54,690.0	29.7	4.9	784,053
	Ningxia Hui Autonomous Region	4,778.0	29.7	4.9	115,039
	Shanxi Province	24,916.0	29.7	4.9	456,142
Semi-humid plains of northeast China	Heilongjiang Province	26,732.0	44.9	6.6	327,560
	Liaoning Province	31,656.0	44.9	6.6	249,428
	Jilin Province	17,970.5	44.9	6.6	149,116
Semi-humid plains of Yellow, Huai and Hai Rivers	Beijing City	5,038.0	35.6	15.7	22,162
	Tianjing City	6,458.0	35.6	15.7	100,505
	Hebei Province	63,424.0	35.6	15.7	1,097,496
	Shandong Province	148,190.0	35.6	15.7	2,607,608
	Henan Province	61,525.0	35.6	15.7	960,380
Mountain and hilly areas of south China	Anhui Province	35,030.0	35.6	15.7	502,927
	Jiangsu Province	35,308.0	35.6	15.7	493,807
	Zhejiang Province	24,096.0	18.1	8.5	148,070
	Fujian Province	35,802.0	18.1	8.5	122,095
	Guangdong Province	19,569.0	18.1	8.5	113,174
	Guangxi Zhuang Autonomous Region	21,632.0	18.1	8.5	305,508
	Hainan Province	6,815.0	18.1	8.5	33,893
	Guizhou Province	19,838.0	18.1	8.5	226,611
	Yunnan Province	58,272.0	18.1	8.5	724,828
	Shanghai City	7,121.0	18.1	8.5	32,592
Humid plains of south China	Jiangxi Province	24,916.0	18.1	8.5	134,631
	Chongqing City	18,257.0	35.4	9.3	341,118
	Sichuan Province	71,026.0	35.4	9.3	832,042
	Hubei Province	33,002.0	35.4	9.3	516,890
	Hunan Province	49,328.0	35.4	9.3	687,498
Arid and semi-arid plains of northwest China	Tibet	389.0	52.7	16.2	2,865
	Qinghai	515.0	52.7	16.2	6,865
	Xinjiang Uygur Autonomous Region	149,114.0	52.7	16.2	2,037,660

^a Residual rate = (total residual amount of plastic film in soil after harvest – residual amount of plastic film before mulching)/total amount of mulching plastic film used

into the soils after plastic film mulching, with pollution loads of 19.8, 17.5, 14.0, 13.3 and 13.0 kg/ha/year PAEs, respectively. This is in relation to the intensity of agricultural mulching activity in these provinces, suggesting that higher pollution load of PAEs occur in the provinces that are well known for their use of mulching in agricultural production.

The highest pollution load occurred in Beijing City where very large amounts of plastic film were used for vegetable production to maintain optimum growth conditions. However, under the recycling scenario, only Beijing City, Tibet and Fujian Province reached amounts of more than 5 kg/ha/year of PAEs load. Tibet, which contains fewer greenhouses

Fig. 1 The sub-regions of different F_r value in the agricultural soils in China



with plastic film because of their climate and landscape features, 50.2 tons of PAEs are released with non-recycling and 15.4 tons are released without recycling, respectively. However, high residual rate of mulching plastic film of Tibet led to high pollution load of PAEs in its mulching lands, because of the difficulty in collecting the PVC fragments in this cold and high latitude place. Xinjiang Uygur Autonomous Region and Shandong Province released the highest PAEs after plastic film mulching (more than 10,000 tons in non-recycling scenario and more than 5,000 tons in recycling scenario), but only presented 9.4 and 2.9 kg/ha/year of PAEs load in soils for Xinjiang as well as 5.0 and 2.2 kg/ha/year for Shandong in non-recycling scenario and in recycling scenario, respectively. Large land area could be the main reason for these differences. Since the plastic film pollution is common in Chinese agricultural fields, with contamination levels ranging from 60 to 90 kg/ha (Yan et al. 2006), agricultural soil polluted by PAEs load is therefore ubiquitous.

Contamination levels of PAEs in Chinese soils

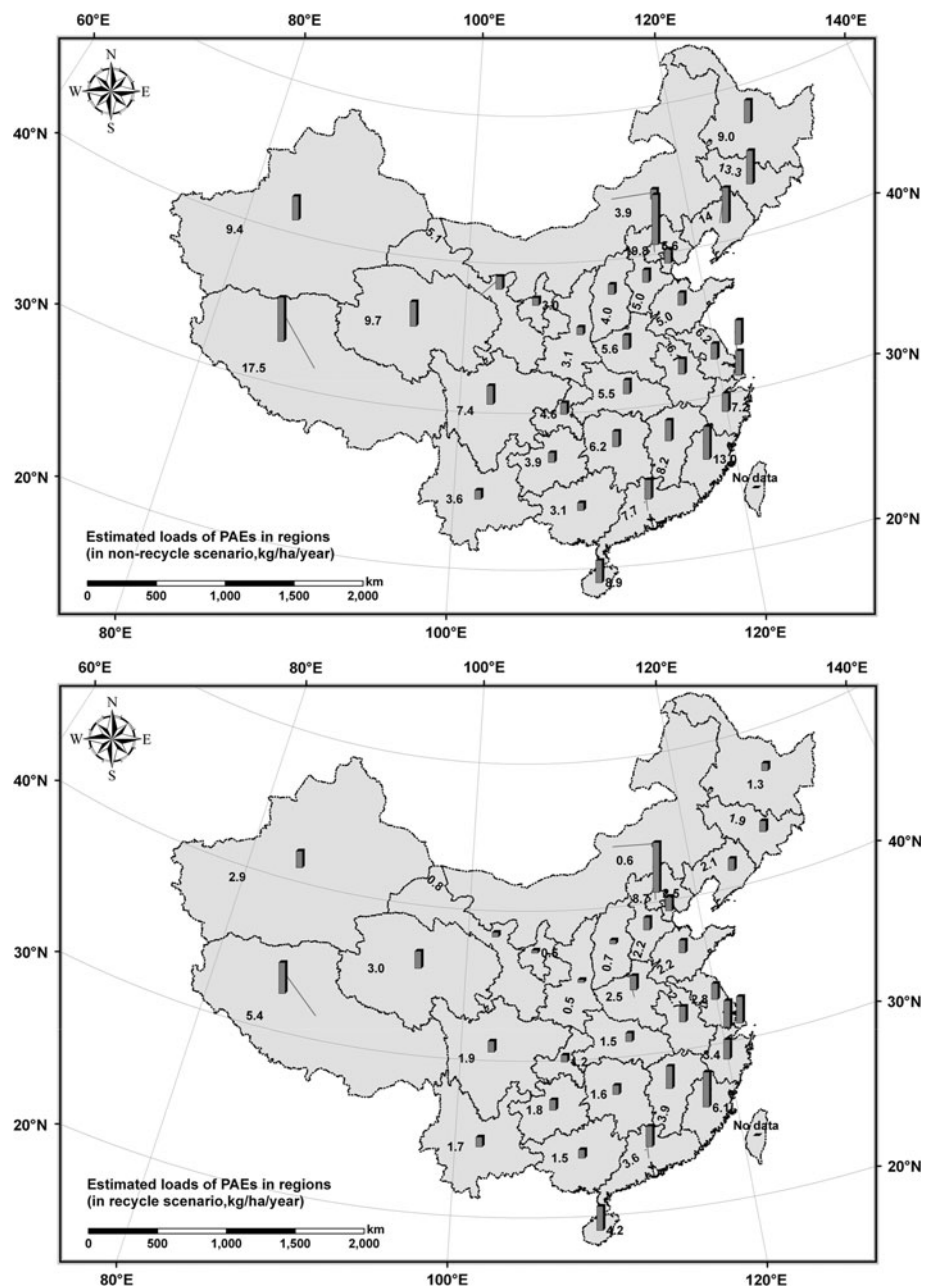
All the PAEs released from mulching plastic film can be expected to enter the soils if it is assumed that there is no degradation or transfer during release. Thus, the contamination levels of PAEs in soils in different provinces (or cities) has been estimated based on the pollution loads presented in Fig. 2. As with the pollution load estimation, estimates of PAE contamination levels also depend on film management (recycling or non-recycling) after mulching (Fig. 3). With recycling, Fujian Province and Beijing City were contaminated badly by PAEs, with the pollution levels of 2.1 and 2.9 mg/kg, respectively. However,

without recycling, contamination levels of PAEs in soils of 14 provinces (or cities) in 31 areas studied were estimated to be greater than 2.0 mg/kg, reaching 5.8 and 6.6 mg/kg, respectively, for Tibet and Beijing City. In addition, the contamination levels (Fig. 3) in the mulching fields from 31 provinces (or cities) were estimated to be more than 1.0 mg/kg under non-recycling compared with those exceeding 1.0 mg/kg with recycling from only 8 areas (Zhejiang, Guangdong, Jiangxi, Hainan, Shanghai, Tibet, Fujian and Beijing). Therefore, plastic film management was effective to control PAE contamination in soils. Unfortunately, little attention is paid to this effective control measure, leading to high PAE contamination levels in most Chinese agricultural soils (Hu et al. 2003; Ma et al. 2003; Zeng et al. 2008). The predicted concentrations of PAEs in soils exceed the target value for soils from Netherlands (Σ PAEs = 0.1 mg/kg; Carlon 2007), indicating very high contamination of most Chinese agricultural soils with plastic film residues. In addition, many sources of PAEs other than plastic film such as sewage sludge application, disposal of other plastic products and atmospheric deposition can also introduce PAEs into soils (Bauer and Herrmann 1997; Cai et al. 2007; Zeng et al. 2010), resulting in more serious situation of PAEs contamination in Chinese agricultural soils.

Discussion

Mulching plastic film residues produce negative impacts on soil physical properties and crop growth and also introduce harmful pollutants into soils that may impact on ecosystem

Fig. 2 Pollution load of PAEs released from mulching plastic film residues in agricultural land in China



or human health. PAEs are important contaminants derived from mulching plastic film residues because of their common and large-scale use as plasticizers in PVC film. Moreover, freely mobile and leachable phase PAEs in PVC products enhance PAE release from the residues of plastic films (Amato et al. 2001; Gómez-Hens and Aguilar-Caballeros 2003; Colombani et al. 2009). As a result, ubiquitous PAE pollution occurs in agricultural land mulched with plastic film (Ma et al. 2003; Chen et al. 2011). Very large amounts of plastic film were used to improve cultivation conditions in China, leading to high contamination levels of mulching plastic film residues in agricultural fields (Wu 1994; Wang 1998; Xu et al. 2005; Yan et al. 2006).

Therefore, high concentrations of PAEs in soils were assumed to originate from applications of larger amounts of plastic film (Hu et al. 2003). In parallel with this situation, the pollution load and contamination levels of PAEs in soils, estimated by the model, were attributable to the amount of plastic film used and the residue rate of plastic film following its utilization.

Those areas where larger amounts of plastic film are used will have higher residues, resulting in higher pollution load and higher PAE contamination levels in the soil. However, pollution load and levels are largely controlled by film management scenario after application (recycling versus non-recycling). Much lower pollution load and

Estimated concentrations of PAEs in soil (in non-recycle scenario, mg/kg)

Region/Province	Estimated Concentration (mg/kg)
Qinghai	3.1
Tibet	5.8
Xinjiang	3.2
Inner Mongolia	1.3
Beijing	1.0
Shanxi	1.9
Hebei	1.8
Shandong	2.1
Henan	1.3
Hubei	1.2
Guangdong	1.0
Guangxi	2.5
Yunnan	1.5
Sichuan	2.5
Chongqing	1.0
Shaanxi	1.3
Shanxi	1.9
Hebei	1.8
Shandong	2.1
Henan	1.3
Hubei	1.2
Guangdong	1.0
Guangxi	2.5
Yunnan	1.5
Sichuan	2.5
Chongqing	1.0
Shaanxi	1.3
Shanxi	1.9
Hebei	1.8
Shandong	2.1
Henan	1.3
Hubei	1.2
Guangdong	1.0
Guangxi	2.5
Yunnan	1.5
Sichuan	2.5
Chongqing	1.0
Shaanxi	1.3
Shanxi	1.9
Hebei	1.8
Shandong	2.1
Henan	1.3
Hubei	1.2
Guangdong	1.0
Guangxi	2.5
Yunnan	1.5
Sichuan	2.5
Chongqing	1.0
Shaanxi	1.3
Shanxi	1.9
Hebei	1.8
Shandong	2.1
Henan	1.3
Hubei	1.2
Guangdong	1.0
Guangxi	2.5
Yunnan	1.5
Sichuan	2.5
Chongqing	1.0
Shaanxi	1.3
Shanxi	1.9
Hebei	1.8
Shandong	2.1
Henan	1.3
Hubei	1.2
Guangdong	1.0
Guangxi	2.5
Yunnan	1.5
Sichuan	2.5
Chongqing	1.0
Shaanxi	1.3
Shanxi	1.9
Hebei	1.8
Shandong	2.1
Henan	1.3
Hubei	1.2
Guangdong	1.0
Guangxi	2.5
Yunnan	1.5
Sichuan	2.5
Chongqing	1.0
Shaanxi	1.3
Shanxi	1.9
Hebei	1.8
Shandong	2.1
Henan	1.3
Hubei	1.2
Guangdong	1.0
Guangxi	2.5
Yunnan	1.5
Sichuan	2.5
Chongqing	1.0
Shaanxi	1.3
Shanxi	1.9
Hebei	1.8
Shandong	2.1
Henan	1.3
Hubei	1.2
Guangdong	1.0
Guangxi	2.5
Yunnan	1.5
Sichuan	2.5
Chongqing	1.0
Shaanxi	1.3
Shanxi	1.9
Hebei	1.8
Shandong	2.1
Henan	1.3
Hubei	1.2
Guangdong	1.0
Guangxi	2.5
Yunnan	1.5
Sichuan	2.5
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Hubei	1.2
Guangdong	1.0
Guangxi	2.5
Yunnan	1.5
Sichuan	2.5
Chongqing	1.0
Shaanxi	1.3
Shanxi	1.9
Hebei	1.

contamination levels occurred under recycling management, indicating that recycling is an effective way to control PAE pollution in agricultural soils. However, soil pollution by PAEs can occur from numerous anthropogenic sources such as sewage sludge application, irrigation with polluted water and disposal of other plastic products (Bauer and Herrmann 1997; Cai et al. 2007; Wang et al. 2008). In addition, atmospheric deposition and fertilizer application can also introduce PAEs into the soil (Mo et al. 2008; Zeng et al. 2010). As a result, the contamination levels of PAEs estimated by the model were lower than previously determined values in Chinese agricultural soils, especially under recycling management (Fig. 4). Moreover, the contamination levels from mulching plastic film under field conditions will be much lower than the predicted values because PAE release from mulching plastic film is a slow process, and degradation and migration usually occur during the release process (Zheng et al. 2007; Xu et al. 2008). It is therefore important to ensure that all sources of PAE pollution in agricultural soils should be identified and quantified in future studies to improve model predictions.

Summary and conclusions

The current study presented a simple model to calculate the pollution load and contamination levels of PAEs in agricultural land from plastic film mulching. The results indicate that the pollution loads and contamination levels of soils in different provinces (or cities) were dependent on the amount of plastic film used and its residue rate in the field. However, whether the film is recycled or not recycled can dramatically affect the estimates, resulting in much lower pollution loads or contamination levels with recycling management. When recycling is not practised, pollution loads with more than 10 kg/ha/year of PAEs can be presented in the soils of Beijing City, Tibet, Liaoning Province, Jilin Province and Fujian Province. However, with recycling, only Beijing City, Tibet and Fujian Province reached amounts of more than 5 kg/ha/year of PAEs load. Under the non-recycling scenario, contamination levels of PAEs in soils of 14 provinces (or cities) in 31 areas studied were estimated to be greater than 2.0 mg/kg, reaching 5.8 and 6.6 mg/kg, respectively, in Tibet and Beijing City. Under the recycling scenario only Fujian Province and Beijing City were estimated to be greater than 2.0 mg/kg. Comparing with the target value for soils of Netherlands (Σ PAEs = 0.1 mg/kg), all the agricultural soils from the studied areas presented high environmental risk to soil ecosystems. Moreover, the contamination levels of PAEs estimated by the model were lower than previous levels detected in Chinese agricultural soils, especially with recycling of plastic film, indicating serious situation of PAEs contamination in Chinese agricultural soils.

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