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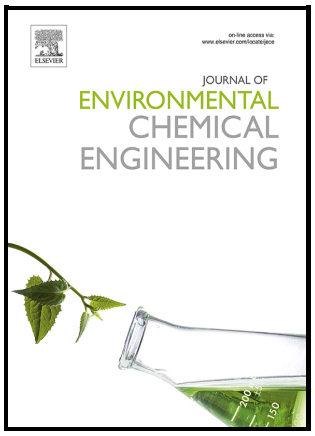

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Occurrence, sources, and risk assessments of phthalic acid esters in tea plantations in China

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Abstract

Phthalic acid esters (PAEs) are one of the most researched and controversial chemicals in recent years due to their widespread distribution in various environmental mediums. However, the status and environmental risks of PAEs in tea plantation soils remain unclear. In this study, the occurrence, sources, and potential risks of dimethyl phthalate (DMP), diethyl phthalate (DEP), diisobutyl phthalate (DiBP), di-n-octyl phthalate (DOP), and di-(2-ethylhexyl) phthalate (DEHP) in 38 tea plantation soils in China were investigated. Results showed that the total concentration of ∑PAEs ranged from 0.002 mg kg^{-1} to 10.90 mg kg^{-1}, with a mean concentration of 1.04 mg kg^{-1}. DEHP (range: ND–9.34 mg kg^{-1}, mean: 0.91 mg kg^{-1}) was the major congener in tea plantation soils, followed by DiBP (range: ND–1.56 mg kg^{-1}, mean:

0.12 mg kg^{-1}). The highest ∑PAEs content in tea plantation soil was observed in Shandong Province, Eastern China. The potential sources of PAEs in tea plantation soils were believed to be plastic films and fertilizers. The non-cancer risk of PAEs was acceptable (< 1). However, the DEHP in 68.42% soil samples posed potential cancer risks (> 10^{-6}) to humans through the dietary route. The DiBP in 10.53% soil samples and DEHP in 5.26% soil samples may cause ecological risks (> 1) to the ecosystem. Thus, long-term continuous agricultural inputs could increase the DEHP and DiBP residues in tea plantation soils, thereby posing potential health risks and ecological risks. Effective measures must be taken to cut off possible sources of DEHP and DiBP in tea plantation soils or reduce their spread from soil to tea plants or food crops.

Keywords:

phthalic acid esters; tea plantation; potential sources; health risks; ecological risks

1. Introduction

Phthalic acid esters (PAEs) are known as emerging contaminants and endocrine disrupting compounds, and they have become ubiquitous due to their extensive application in industry and agricultural production (Das *et al*., 2020). However, during the manufacture, use, and disposal process of plastic products, such as plastic films, wrapping materials, conveyor belts, toys, personal care products, car care products, and medical devices (Škrbić *et al*., 2016; Das *et al*., 2020), PAEs could easily be released into the environments (Benjamin *et al*., 2015; Gao *et al*., 2018). Some PAEs, such as dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DnBP), di-n-octyl phthalate (DnOP), di-(2-ethylhexyl) phthalate (DEHP), and butylbenzyl phthalate (BBP), have already been categorized as

priority-controlled pollutants by many countries and restricted for usage (Das *et al*., 2020). Nevertheless, they have been detected in soil, air, water, sediment, and biota in recent studies (Lee *et al*., 2019; Cheng *et al*., 2020; He *et al*., 2020; Ma *et al*., 2020; Zeng *et al*., 2020).

Soil is the important reservoir of pollutants due to the strong adsorption capacity of soil particle surface. Concerning national food security, numerous scholars have investigated the occurrence and health risks of PAEs in agricultural soils throughout China, including plastic greenhouse (Chai *et al*., 2014; Wang *et al*., 2015; Sun *et al*., 2016), vegetable field (Sun *et al*., 2016; Li *et al*., 2016a; Tao *et al*., 2020), paddy field (Li *et al*., 2015; Wang *et al*., 2017), cotton field (Peng *et al*., 2018), orchard (Liu *et al*., 2013; Li *et al*., 2015), tobacco field (Yu *et al*., 2018; Song *et al*., 2020), and melon field (Mahebali *et al*., 2020). Abundant data manifested the unabated accumulation of PAEs in Chinese agricultural soils due to the constant application of plastic films, fertilizers, pesticides, and sewage sludge (Mo *et al*., 2008; Lü *et al*., 2018). Many toxicology studies demonstrated that PAEs in soils could be taken up by different plants (Cai *et al*., 2015; Sun *et al*., 2015; Wang *et al*., 2015; Zhao *et al*., 2015; Cheng *et al*., 2020), thus affecting the growth of crops, reducing their yield and quality, and finally threatening human health through the food chain.

However, information about the occurrence of PAEs in tea plantation soils is rare. Tea (*Camellia sinensis* L.), one of the top three beverages in the world, is rich in tea polyphenols, proteins, amino acids, vitamins, and mineral elements, and it is widely planted in the tropical and subtropical areas of China (Cao *et al*., 2018). As the largest tea producer and exporter (Tan *et al*., 2019), the total tea plantation area of China reached approximately 3.2 million ha, and the yield exceeded 2.9 million tons in 2020 (NBSC, 2021). Over the recent years, in order

to satisfy the demand of domestic market and need of export, the application of fertilizers and plastic mulching films has become universal in tea planting to increase tea production and quality (Cao *et al*., 2018; Zhang *et al*., 2020). Previous studies demonstrated that a relatively high level of PAEs content (0.03–2.24 mg kg^{-1}), which derived from agricultural activities instead of plastic packaging, was detected in fresh tea leaves (Yin *et al*., 2014; Liu *et al*., 2016). Liao *et al*. (2019) indicated that the total concentrations of PAEs ranged from 1.33 mg kg^{-1} to 2.77 mg kg^{-1} in tea plantation soils through the use of fertilizers and pesticides in West Lake, Hangzhou. Thus, PAEs contamination in tea plantation soils could lead to the bioaccumulation of PAEs in teas, and then transferred to human body by dermal contact, adsorption, inhalation, and ingestion (Wang *et al*., 2015). Studying the spatial distribution, source analysis, and risk assessment of PAEs is particularly vital for tea plantations. In addition, the soil environment of tea plantation is different from other types of agricultural soils. Tea plant prefers acidic soils and special trace metals (Cao *et al*., 2018). Decreasing pH value; leaching of nutrients; and accumulation of aluminum, fluorine, chlorine, calcium, and magnesium in tea plantation becomes detrimental to the growth and quality of tea trees (Gu *et al*., 2019; Yang *et al*., 2019). Meanwhile, soil pH, organic matter content, and the specific surface area of clay minerals affect the accumulation of PAEs (Li *et al*., 2016b). However, the correlations between soil properties and accumulation of PAEs in tea plantation remain poorly understood.

Therefore, this study aimed to 1) investigate the occurrence, potential sources, and risks of PAEs in different Chinese tea plantation soils; 2) discuss the main factors affecting PAEs residues, along with soil properties; and 3) enrich the foundation database for PAEs pollution

and promote the sustainable development of agriculture in China.

2. Materials and methods

2.1. Sample collection

A total of 114 soil samples in 38 tea plantations were collected from 13 provinces (Shandong, Jiangsu, Zhejiang, Jiangxi, Auhui, Fujian, Hunan, Hubei, Guangdong, Guangxi, Sichuan, Guizhou, Yunnan) in four regions, including East, Central, South, and Southwest China, from July 2017 to September 2017. The tea plantations were distributed in the warm temperate zone, subtropical zone, and tropical zone (21.9° N–36.3° N, 98.5° E– 120.6° E). The annual average temperature and precipitation ranged from 12 °C to 22 °C and from 700 mm to 2600 mm, respectively, and the altitude ranged from 0 m to 1899 m. There were 1 – 4 tea plantations where covering films selected for each province. The detailed information and locations of the sampling sites are shown in the Supporting Information (Table S1 and Fig. S1). First, the interfering substances on the soil surface was removed. Then, five kilograms soils (0–20 cm) were collected with a wooden scoop by a five-point sampling method (inside a square with a side of length 10 m) and mixed to form a single sample. Three parallel soil samples were collected from each tea plantation by using the same method. The soil samples were packed in cloth bags and immediately transported to the laboratory by ice boxes. All the samples were stored at −4 °C for soil physicochemical property analysis, including soil pH, total organic carbon (TOC), total N (TN), ammonium (NH_4^+), nitrate (NO_3^-), P, S, Cl, K, Ca, Na, Mg, Al, Fe, and Si. A ^{15}N tracing technique was used to investigate the rate of nitrogen transformation according to the methods described by Müller *et al*. (2003) and Zhu *et al*.

(2014). Soil samples were freeze-dried in vacuum and sieved using a 0.25 mm nylon sieve before analysis.

2.2 Sample extraction and cleanup for PAE analysis

A standard mixture of DMP, DEP, DnBP, diisobutyl phthalate (DiBP), BBP, DEHP, DnOP and the surrogate standard DnBP-d4 were purchased from Dr. Ehrenstorfer (Augsburg, Germany). The high-performance liquid chromatography grade n-hexane and ethyl acetate were purchased from Sigma Chemical Corporation (St. Louis, MO).

For each sample, 1.0 g soil was placed into a glass conical flask, mixed with 15 mL ethyl acetate/n-hexane (1:1, v/v), and then ultrasonically extracted for 30 min after shaking for 1 min, followed by centrifugation at 3200 r min^{-1} for 9 min. The supernatant was collected, and the procedure was repeated three times. The merged extracts were combined into a round-bottom flask, concentrated by rotary evaporation to 1 mL, and then transferred to a graduated tube. The round-bottom flask was washed with n-hexane three times. The n-hexane wash was transferred to the above graduated tube and diluted with n-hexane to 5 mL. The extract (1 mL) was removed into a centrifuge tube and cleaned by centrifugation at 14000 r min^{-1} for 13 min. One-hundred μL supernatant was transferred into the chromatographic bottle. Finally, 10 μL internal standard (DnBP-d4) was added and diluted to 1 mL by using n-hexane for instrumental analysis.

The quantitative analysis of PAEs was carried out by an Agilent 7890GC-5975MSD gas chromatography-mass spectrometry (GC-MS, Agilent Technologies, Palo Alto, CA) equipped with a DB-5 trace analysis column (30 m × 0.25 mm × 0.25 μm) fused-silica capillary column for chromatographic separation. The GC oven temperature was held at 50 °C for 1 min,

programmed to increase at 15 °C min^{-1} to 200 °C for 1 min, and finally held at 280 °C at 8 °C min^{-1} for 3 min. One 1 μL of each extract was injected into the GC-MS system in non-pulse and splitless mode with an injector temperature of 250 °C. The temperatures of the transfer line and the electron capture detector were 280 °C and 300 °C, respectively.

2.3 Quality assurance and quality control

Before use, all glassware was immersed in potassium dichromate solution overnight, washed with pure water, and rinsed with n-hexane. No plastic vessels were employed in the experimental procedures. Instrument blank, solvent blank, and triplicate sample detection for each batch of samples were performed to reduce the interference of the background blank value. Procedural blanks were run every 12 samples. Trace DiBP and DEHP were detected in procedural blanks and subtracted from the measured concentrations. As shown in Table S2, the recovery rates of seven PAEs and surrogate standard in the spiked matrix blank samples ranged from 73.5% to 112.1% and from 78.6% to 107.4%, respectively, where relative standard deviation (RSD) was < 15% (n = 6). The method detection limits (MDL) of the seven PAEs were 0.01–0.39 μg kg^{-1}. The instrumental detection limits were calculated by a signal-to-noise ratio three times the sample concentration, and they ranged from 0.13 μg L^{-1} to 0.51 μg L^{-1}. When the detected data were below the MDL value, half of the MDL value was used to perform statistical analysis.

2.4 Health risk assessments

The health risks of PAEs to adults and children were estimated in accordance with the methods recommended by USEPA (2013). DMP, DEP, DnBP, and DnOP were recognized as non-cancer-related compounds, while BBP and DEHP presented cancer risk. DiBP and DnBP

have been reported to show similar toxicology effects (NRCNA, 2008). Therefore, the non-cancer risk of DiBP was evaluated using the RfD (Reference Dose) and BAF (Bioaccumulation Factor) values of DnBP in the present study. The non-cancer and cancer risk assessments of PAEs via diet (only considering the intake of vegetables grown in soils) and non-dietary (soil ingestion, dermal contact, and inhalation) routes were calculated as follows:

$$ADD_{\text{dietary}} = \frac{CS \times BAF \times IRF \times EF \times ED}{BW \times AT} \times CF \quad (1)$$

$$ADD_{\text{ingest}} = \frac{CS \times IRS \times EF \times ED}{BW \times AT} \times CF \quad (2)$$

$$ADD_{\text{dermal}} = \frac{CS \times SA \times AF \times ABS \times EF \times ED}{BW \times AT} \times CF \quad (3)$$

$$ADD_{\text{inhale}} = \frac{CS \times EF \times ED \times I_j}{PEF \times AT} \times 10^3 \quad (4)$$

$$ADD_{\text{non-dietary}} = ADD_{\text{ingest}} + ADD_{\text{dermal}} + ADD_{\text{inhale}} \quad (5)$$

$$CR = \Sigma(ADD_i \times CFS) \quad (6)$$

$$HQ = \Sigma(ADD_i / RfD) \quad (7)$$

Where CS is the target phthalate in soil (mg kg^{-1}); ADD_i (mg kg^{-1} d^{-1}) is the average daily dose via dietary (ADD_{dietary}, food intake) and non-dietary (ADD_{ingest}, ADD_{dermal}, ADD_{inhale}, soil

ingestion, dermal contact, and inhalation) routes; *CR* is the cancer risk (unitless); and *HQ* is the hazard quotient to quantify the non-cancer risk. $CR > 10^{-6}$ indicates cancer risk, but cancer risk is acceptable when $10^{-6} < CR < 10^{-4}$. $HQ < 1$ indicates no significant risk of non-cancer effects, and $HQ > 1$ indicates the non-cancer effects. Other parameters are presented in Table S3.

2.5 Potential ecological risk assessment

No unified standard of ecotoxicological risk assessment for PAEs exists. Risk quotient (*RQ*) was used to evaluate the ecotoxicological risk of chemicals to ecosystems (Wang *et al*., 2016b). It was calculated by the measured environmental concentration (MEC) in soil and the environmental risk limits (ERL).

$$RQ = MEC/ERL \quad (8)$$

The ERL values (mg kg^{-1}) were represented by the ecological soil screening levels (DMP: 0.35; DEP: 0.25; DnBP: 0.01; DnOP: 0.91; DEHP: 0.02) for terrestrial wildlife (US EPA, 2018). The ecotoxicological risk of DiBP was evaluated using the ERL values of DnBP. The *RQ* values were divided into two levels of risk: no ecotoxicological risk (< 1) and ecotoxicological risk (> 1).

2.6 Statistical analysis

R version 3.6.3 was used for data analysis. Normality of data was examined by Shapiro–Wilk test. T test was used to compare the differences in normally distributed data. Given that data were not normally distributed, a nonparametric two–sample Mann–Whitney U test and a multivariate nonparametric several–sample Kruskal–Wallis test were applied to detect the

differences of independent samples. The level of statistical significance was set at $p < 0.05$. Spearman correlation analysis was performed to assess the correlations among variables.

3. Results and discussion

3.1 Occurrence of PAEs in tea plantation soils

The concentration for all detected PAEs in tea plantation soil is presented in Table S4. DnBP and BBP were not detected in all soil samples of this study. The total concentrations of PAEs (ΣPAEs) in tea plantation soils across China extended over 2–3 orders of magnitude, ranging from 0.002 mg kg^{-1} to 10.90 mg kg^{-1}, with a mean value of 1.04 mg kg^{-1} and a median value of 0.34 mg kg^{-1}, representing a right skewed distribution (Shapiro–Wilk test, $p < 0.05$, skewness = 3.71, kurtosis = 15.56). The variation coefficient was as high as 191%. As shown in Fig. 1, the highest level of PAEs was observed in the tea plantation soils of Shandong Province (mean: 6.64 mg kg^{-1}). The tea plantations in Jiangsu Province (mean: 1.12 mg kg^{-1}) and Fujian Province (mean:1.11 mg kg^{-1}) also showed higher levels of PAEs in soils. Therefore, the mean value of ΣPAEs in tea plantation soils in Eastern China (1.85 mg kg^{-1}) was significantly higher than that in Southwest (0.74 mg kg^{-1}), Southern (0.10 mg kg^{-1}), and Central (0.35 mg kg^{-1}) China (Mann-Whitney U test, $p < 0.05$, Table 1). In terms of each sampling site, the highest ΣPAEs concentration in soils was observed in SD1 (Table S4), with a mean value of 10.90 mg kg^{-1}. The lower ΣPAEs concentrations in soils were occurred in GX2 and HB3, and the mean concentrations were approximately 0.01 mg kg^{-1}.

The residue of PAEs in different types of agricultural soils has aroused wide public concern in recent years. Previous works revealed that the ΣPAE values in Chinese arable soils ranged from 0.89 mg kg^{-1} to 10.0 mg kg^{-1} (mean: 3.43), as reported by Hu *et al*. (2003); from 0.08

mg kg^{-1} to 6.37 mg kg^{-1} (mean: 1.09), as reported by Niu *et al*. (2014); and from 0.04 mg kg^{-1} to 7.54 mg kg^{-1} (mean: 1.37), as reported by Sun *et al*. (2018). Higher levels were tested from Northern China than from Southern China, similar to the result of this present study. Tea is a tropical plant grown in warm and humid environments (Zhang *et al*., 2020). According to the survey shown in Table S1, plastic film mulching has been used to improve soil temperature, and enhance water and nutrients use efficiency, especially in Eastern China (like Shandong Province, Jiangsu, Fujian) or Southwest China (like Yunnan Province) areas. In addition, the usage amounts of agricultural plastic films in Shandong, Sichuan, Yunnan, and Jiangsu Province in 2016 were ranked in the top 10 in China (NBSC, 2017). Therefore, the PAEs value in the tea plantation soils from Shandong Province was well over the abovementioned national average, which may be correlated with the application of plastic films. Affected by the long history of greenhouse vegetable planting, the PAEs values in mulching soils in Shandong Province were as high as 35.44 (Chai *et al*., 2014) and 18.81 (Li *et al*., 2016b) mg kg^{-1}, which depended on the non-covalent interaction with the plastic matrix (Gao *et al*., 2018). Other studies revealed a broad range of PAEs content (0.03–12.1 mg kg^{-1}) in greenhouse soils in Yangtze River Delta cities, Eastern China (Chen *et al*., 2011; Wang *et al*., 2013; Sun *et al*., 2016). Therefore, PAE contamination was considered closely connected to the extent of plastic film mulching. Meanwhile, a low level of PAEs residue (0.01–2.46 mg kg^{-1}) still remained under the advantageous hydrothermal condition in subtropical and tropical areas in this study, where the usage amounts of plastic films was low. This finding may be explained by the application of fertilizers, involving chemical fertilizer, organic fertilizer, and compound fertilizer. The fertilizer consumption varied from 25 kg ha^{-1} to 2 tons

ha^{-1} in 38 tea plantations in 2016 (Table S1). Previous investigations indicated that the PAEs content in chemical and organic fertilizers were 0.01–2.80 (Mo *et al*., 2008) and 2.24–6.84 (Wang *et al*., 2013) mg kg^{-1}, respectively. The higher application rates of fertilizers may lead to higher PAEs accumulation in soil (Lü *et al*., 2018). These results has been verified by studies from subtropical vegetable soils, such as in Guangzhou (0.20–33.59 mg kg^{-1}, Zeng *et al*., 2008) and Pearl River Delta (3.00–45.67 mg kg^{-1}, Cai *et al*., 2005).

In summary, the PAEs contamination in tea plantation soils in China was on moderate level with high spatial heterogeneity. Continuous agrochemical input plays a critical role in the soil PAEs accumulation. Protecting soil environment is vital to tea quality and human health, as well as economic development and national ecological security. Therefore, controlling the pollution sources of emerging contaminants is considerably urgent.

3.2 Composition of PAEs in tea plantation soils

Despite the significant difference among the individual PAEs concentration, the composition of PAEs in soils was similar (Fig. 1). The detection rates of DEHP, DiBP, DMP, DOP, and DEP were 97.36%, 89.47%, 55.26%, 44.74%, and 7.89%, respectively. DEHP was the major congener in 36 tea plantation soils expect HB3 and GX2, with contributions of 76.26%–97.01%. DiBP (ND–1.56 mg kg^{-1}) was a relatively minor congener, with a mean concentration of 0.12 mg kg^{-1} in soils, accounting for 0%–16.67%. The contents of DMP, DEP, and DOP were all relatively low (Table 1). Compared with the guidelines recommended by the US EPA (US EPA, 2013), only the content of DEHP in tea plantation soils collected from SD1 and SD2 exceeded the allowable concentration (4.35 mg kg^{-1}), posing a potential threat.

The results shown in Table 2 illustrated the occurrence of DEHP and DiBP in Chinese agricultural soils. The average concentrations of DEHP (0.82 mg kg^{-1}) and DiBP (0.07 mg kg^{-1}) in arable soils across China (Niu *et al*., 2014) were lower than those of the present study. Compared with other types of agricultural soils, the DEHP concentration in tea plantations soils of the present study was higher than that in paddy field (Li *et al*., 2015; Wang *et al*., 2017), tobacco field (Yu *et al*., 2018; Song *et al*., 2020), cotton field (Peng *et al*., 2018), and melon field (Mahebali *et al*., 2020). On the contrary, it was lower than that in greenhouse soils (Chai *et al*., 2014; Wang *et al*., 2015). A relatively high level of DiBP accumulated in tea plantation soils of Eastern China (Table 1), as well as in mulching soils of Shandong Province (Chai *et al*., 2014; Li *et al*., 2016b) and Guangdong Province (Zeng *et al*., 2020). Thus, DEHP and DiBP contaminations were ubiquitous in agricultural soils, especially in mulching soils, exhibiting their prevailing application and persistence (Gao *et al*., 2018).

However, a literature review considered that DEHP and DnBP were the main members of PAEs in different types of agricultural soils (Lü *et al*., 2018). Sun *et al*. (2016) demonstrated that DEHP and DnBP were the major pollutants in the arable soils of Eastern China. In the tea plantation soils of the West Lake, DEHP and DnBP has been found as the predominate PAEs congeners, with mean contributions of 57.21% and 30.59%, respectively (Liao *et al*., 2019). The level of DnBP was even found to be higher than that of DEHP in other studies (Chai *et al*., 2014; Li *et al*., 2016b; Song *et al*., 2020). DEHP and DnBP were the most commonly used commercial PAEs (Das *et al*., 2020), but DiBP has been historically used less and thus relatively less studied. In the present study, DiBP potentially had more negative effect on the environment than DnBP. Such finding deserves particular attention, perhaps because of DiBP

being used as a substitute for DnBP when DnBP have already been restricted for use (Yost *et al*., 2019).

3.3 Potential sources analysis

Table 3 lists the Spearman correlation coefficient among individual PAEs. DEHP showed a strong positive relationship with DiBP (R = 0.97, $p < 0.001$), suggesting that these PAEs may have common sources or similar environmental behavior. The results were further confirmed by principal component analysis (PCA, Fig. 2). The results of factors loading with varimax rotation and eigenvalues are outlined in Table S5. Given the few calculated variables, the PCA result only extracted two components with eigenvalues above 1, which contributed to 43.12% and 24.65% of the cumulative variances (Table S5). Thus, the discussion hereafter mostly focused on the two principal components. DEHP and DiBP were mainly loaded in the first component (PC1), indicating that DEHP and DiBP shared a common source in tea plantation soils. According to previous studies, PC1 may manifest the emission of DiBP and DEHP from plastic films and fertilizers (Wang *et al*., 2015; Lü *et al*., 2018). Meanwhile, the second component (PC2) was positively related to DMP and DEP while negatively related to DOP, which may originate from pesticides and wet-dry deposition (Niu *et al*., 2014).

Agricultural chemical inputs played a critical role in PAEs contamination, especially plastic films (Lü *et al*., 2018). DEHP and DiBP were confirmed to be commonly used in flexible polyvinyl chloride production (Das *et al*., 2020). Wang *et al*. (2021) investigated the PAEs concentrations in PVC greenhouse films (140,000–282,000 mg kg^{-1}) and mulch films (2.59–359 mg kg^{-1}) and then reported that DEHP was the main component. On the other hand, DEHP with high molecular weight showed a high value of octanol-water partition coefficient

and high hydrophobicity, and it was difficult to be biodegraded (Zhu *et al*., 2018). Meanwhile, it could be easily absorbed by soil organic matter and then accumulated in soils (Kim and Lee, 2019). In addition, high temperature in summer may accelerate the volatilization rate of medium-molecular-weight PAEs, such as DiBP, suggesting an escape trend from the soils to the atmosphere (Li *et al*., 2020), and thus a low residue level was observed in tea plantation soils of this study. By contrast, DMP and DEP with a short alkyl chain have a high solubility and vapor pressure, employed in solvents of pesticides, personal care products, and cosmetics (Das *et al*., 2020). They were also reported to be easily biodegraded or to migrate from soils to air by evaporation (Kim and Lee, 2019; Li *et al*., 2020). When the rate of input exceeded that of evaporation or microbial degradation, they could accumulate in soils. For instance, the overuse of pesticides and fertilizers made short-chain PAEs, namely, DMP, exhibit the highest concentration in mulching soil, vegetable soil, grassland, and orchard (Tao *et al*., 2020). Although the use of priority-controlled PAEs and the plastic waste emission have been prohibited or reduced by governments, these artificial chemicals could still accumulate in tea plantation soils, which primarily originated from the extent use of agricultural plastic films, fertilizers, and even the regeneration and reuse of waste plastics.

3.4. Relationship between PAEs and soil properties

In this study, the pH values of tea plantation soils ranged from 3.50 to 5.95, with a mean of 4.55. The TOC content varied greatly from 0.35% to 6.92%, with a mean of 1.15%, and the proportion of clay varied from 3.97% to 41.80%. The results of other soil properties is shown in Table S6 and S7. The result in Table 3 showed that DiBP, DEHP, and total PAEs exhibited a significantly positive correlation with the proportion of Na element (R = 0.70, 0.65, and 0.66,

respectively, $p < 0.05$). The other measured soil elements were not correlated with the concentrations of PAEs. Few studies have focused on the relationships between PAEs and trace elements. Soil trace elements usually have steady patterns in the forms of exchangeable cations (such as Al^{3+}, Fe^{3+}, Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+}) or clay minerals (such as Al_2O_3, Fe_2O_3, CaO, MgO, K_2O, and Na_2O). PAEs exposed to strong acid environment could be protonated and then adsorbed by soil particle surface, which depended on soil cation exchange capability (Wagner *et al*., 1994). Thus, the co-occurrence of Na and PAEs may be explained by the greater proportion of soil Na^{+}.

As shown in Fig. 3, the mineralization rate of recalcitrant organic N to NH_4^{+} (M_{Nrec}), the oxidation rate of recalcitrant organic N to NO_3^{-} (O_{Nrec}), and the immobilization rate of NO_3^{-} to recalcitrant organic N (I_{NO3}) were significantly correlated with the content of soil PAEs ($p < 0.05$). Thus, N transformation process may affect soil PAEs accumulation, which connected with soil microbial communities composition and functions. In the previous study, soil properties indirectly affected the occurrence of PAEs in soils by altering the structure and activity of functional microbial communities (Zhu *et al*., 2018; Gu *et al*., 2019). The high rate of N fertilization and low nitrogen use efficiency in tea plantation soil provided a particular niche for soil microbial communities assembly (Zhu *et al*., 2014), and then possibly affect the biodegradation of PAEs. To our knowledge, the relationship of PAEs and N transformation rate is discussed for the first time. On the other hand, Wang *et al*. (2014) found that PAEs altered soil microbial N content and urease activities. Therefore, PAEs pollution may also affect the transformation process of soil organic N, promoting the accumulation of NH_4^{+} and the leaching of NO_3^{-}, resulting in soil acidification and salinization (Yan *et al*., 2020). More

work is needed to investigate soil microbial community structure and function in the future to elucidate the underlying mechanisms.

In addition, soil organic matter has been proven to be a key factor governing the occurrence of PAEs, playing a vital role in the partitioning, storage, and longevity of PAEs. Niu *et al*. (2014) found that PAEs were positively related to soil organic matter, attributed to its strong adsorption capability. However, no significant correlation was observed between TOC and PAEs in the present study. Katsoyiannis (2006) proved that a lack of correlation of TOC and hydrophobic organic chemicals, such as PAEs, should be expected if a continuous input of fresh pollutant exists in an environment. In the present study, agricultural inputs containing abundant PAEs continuously introduced into soils during tea planting, including plastic films, fertilizers, and pesticides, may hinder the achievement of equilibrium between PAEs and TOCs. The lack of correlations between soil organic matter and PAEs was also published in previous studies (Chai *et al*., 2014; Li *et al*., 2016a). Moreover, a poor relationship was observed between pH and PAEs in the present study, contrary to the result reported by Li *et al*. (2016b) and Zhang *et al*. (2018).

3.5 Health risk assessment and ecolotoxicogical risk assessment

Dietary intake was considered here because tea plantations were covered under crop rotation or intercropping measures with other food crops. The results of health risk assessment and ecolotoxicogical risk assessment are summarized in Table 4 and Fig. 4. The mean non-cancer risks (*HQ*) via dietary ($ADD_{dietary}$) and non-dietary ($ADD_{non\text{-}dietary}$) pathways decreased in the order of DEHP, DiBP, DOP, DEP, and DMP, which were all less than 1, and did not pose a threat to adults and children. Dietary intake was the predominant exposure route, accounting

for approximately 99% of the total non-cancer risks, followed by inhalation, soil ingestion, and dermal contact. The *HQ* values for adults were more than twice that for children. Besides, the highest total non-cancer risk was 0.28 for adults and 0.11 for children, respectively, which was observed in SD1 soil samples and close to the threshold. In terms of cancer risks, the mean *CR* values of DEHP in all soil samples via non-dietary routes were within the recommended allowable level (< 10^{-6}). However, the mean CR value of DEHP via dietary route was much higher than 10^{-6} (7.20×10^{-6} for adults and 2.84×10^{-6} for children), and thereby posed a potential cancer risk (Fig. 4). Therefore, the DEHP in 68.42% of soil samples posed potential cancer risks to human through the dietary route. The mean RQ values were arranged in the order of 1 > DiBP > DEHP > DEP > DMP > DOP, which posed no potential ecotoxicological risk to soil wildlife. The DiBP of 10.53% soil samples and the DEHP of 5.26% soil samples may cause ecological risks. Moreover, the RQ values of DiBP and DEHP in SD1 soil samples were both above 1, presenting the greatest threat to the ecosystem. Contrary to the result of health risk assessment, DiBP showed the highest ecological risk.

The result of this study was similar to the health risks of arable soils across China estimated by Niu *et al*. (2014), which showed that DEHP via dietary intake had the highest cancer risk to human health (7.37×10^{-6}), and dietary intake was the largest contributor of different sources of exposure. Most researchers revealed that DEHP via dietary intake presented the greatest cancer risk but a negligible non-cancer risk to human health (Wang *et al*., 2015; Ma *et al*., 2020; Tao *et al*., 2020). In addition, previous biological monitoring experiments reported that DEHP could accumulate in tea leaves (Liu *et al*., 2016) and vegetables (Wang *et al*., 2015; Sun *et al*., 2015; Zhu *et al*., 2019; Cheng *et al*., 2020) and cause harm to human

health through the food chain. Thus, effective measures should be carried out to control the levels of DEHP, which has a great effect on the human reproductive system, respiratory diseases, obesity and diabetes, and neuropsychological disorders (Caldwell, 2012), or reduce its transfer from soil to food crops. Nevertheless, studies on the ecological risk of PAEs in soils were limited. Li *et al*. (2016c) calculated the health risks and ecological risks of PAEs in sediments and identified that DEHP posed high ecological risks but no human health risks. A toxicological study indicated that low-dose DEHP exposure over a long time period may cause more severe damage to soil animals (Li *et al*., 2021). Therefore, the potential ecological risks of DEHP in soil ecosystems could not be ignored because of its remarkable bioaccumulation. Unfortunately, information about the long-term toxicological data of DiBP accumulation in soils is limited. It is a timely reminder to take soil DiBP pollution and the associated ecological risks into consideration due to the high public concern on emerging contaminants. A notable detail that the use of PAEs-containing products in tea plantation soils, particularly in Shandong Province, should be restrained to effectively reduce or eliminate the environmental risk of PAEs and their accumulation in soils and tea plants.

4 Conclusions

In this study, the occurrence, potential sources, and health risks of PAEs in tea plantation soils from Eastern, Central, Southern, and Southwestern China were analyzed. The total concentration of ∑PAEs ranged from 0.002 mg kg^{-1} to 10.90 mg kg^{-1}, with a mean concentration of 1.04 mg kg^{-1}, which was similar to the national average in other previous reports. The highest ∑PAEs content in the tea plantation soils was observed in Shandong Province. DEHP was the major congener in 36 tea plantation soils except HB3 and GX2,

accounting for 76.26%–97.01% of the ∑PAEs concentrations. The primary potential source of PAEs in tea plantation soils may be agricultural plastic films and fertilizers. Health risk assessment demonstrated that non-cancer risk exposed to adults and children was relatively safe. However, DEHP represented the greatest carcinogenic risk to residents through dietary intake, and DiBP displayed higher ecological risks than DEHP. Thus, long-term application of agricultural inputs could threaten the soil ecosystem and increase the health risks of PAEs from drinking tea or intaking food crops grown in risk-related areas. Therefore, effective measures must be taken to control the levels of DEHP and DiBP in tea plantation soils or reduce their transfer from soil to tea plants or food crops.

CRediT authorship contribution statement

Yutong Li: Formal analysis, Visualization, Data Curationt, Writing - Original Draft; **Jun Wang**: Funding acquisition, Project administration, Writing - Review & Editing; **Hongcheng Bai**: Investigation, Writing - Review & Editing; **Kang Ni**: Investigation, Data curation; **Kun Liu**: Investigation, Data curation; **Peili Lu**: Writing - Review & Editing.

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Appendix A. Supplementary data

Supplementary materials

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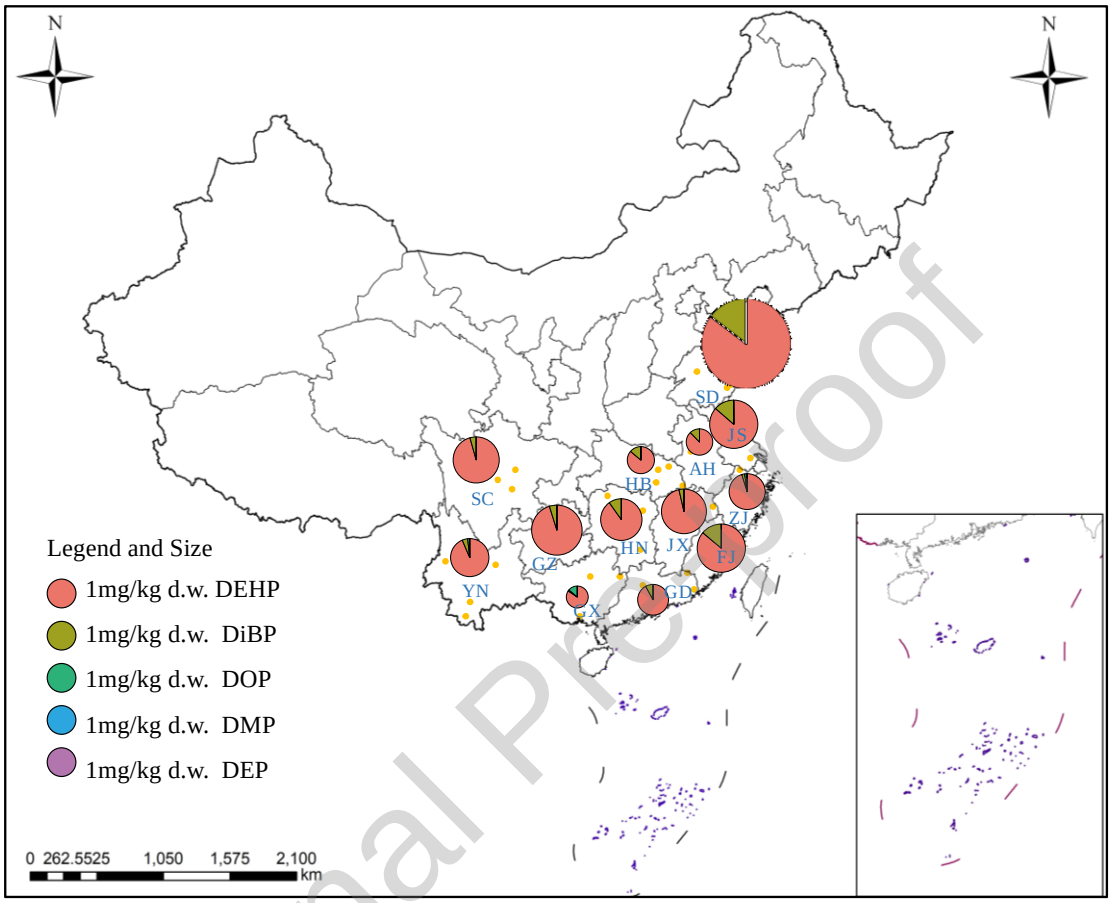


Fig.1 Spatial distributions of PAEs in the tea plantation soils across China, including Shandong (SD), Jiangsu (JS), Zhejiang (ZJ), Anhui (AH), Jiangxi (JX), Fujian (FJ), Hubei (HB), Hunan (HN), Guangdong (GD), Guangxi (GX), Yunnan (YN), Sichuan (SC), and Guizhou (GZ). The percentage composition of each PAEs' monomer was visualized by pie charts. The area of pie chart represented the total content of PAEs in each province.

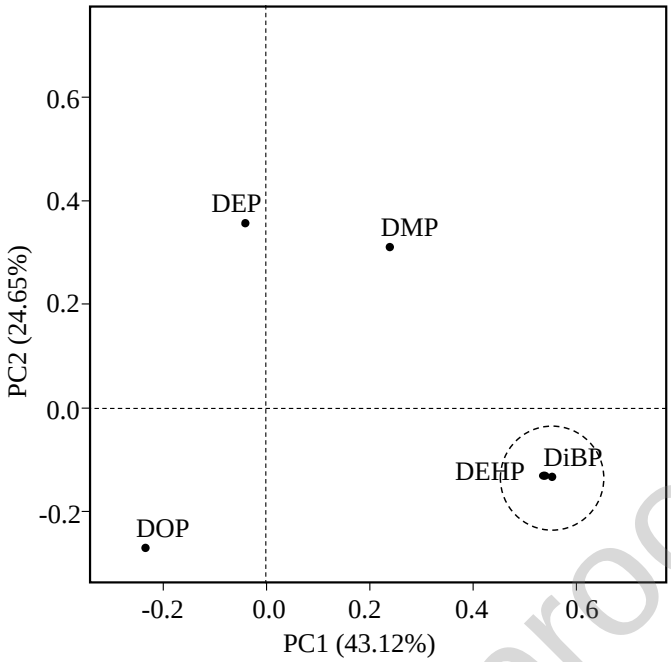


Fig.2 Factor loadings of PAEs congeners of the soils samples on two principal components

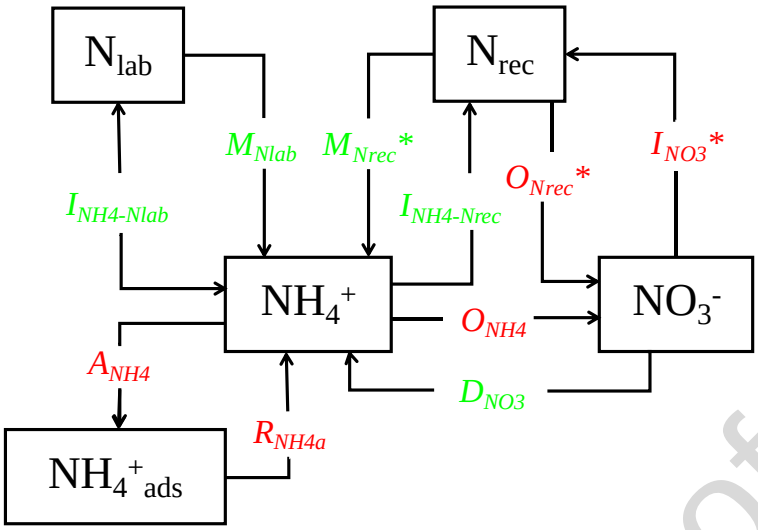


Fig.3 ^{15}N tracing model. (N_{lab} = labile organic N, N_{rec} = recalcitrant organic N, NH_4^+ = ammonium, NO_3^- = nitrate, $NH_4^+{}_{ads}$ = adsorbed NH_4^+; green font indicates positive relationships with PAEs content, red font indicates negative relationships, significant relationship is highlighted by boldface at $p < 0.05$ level).

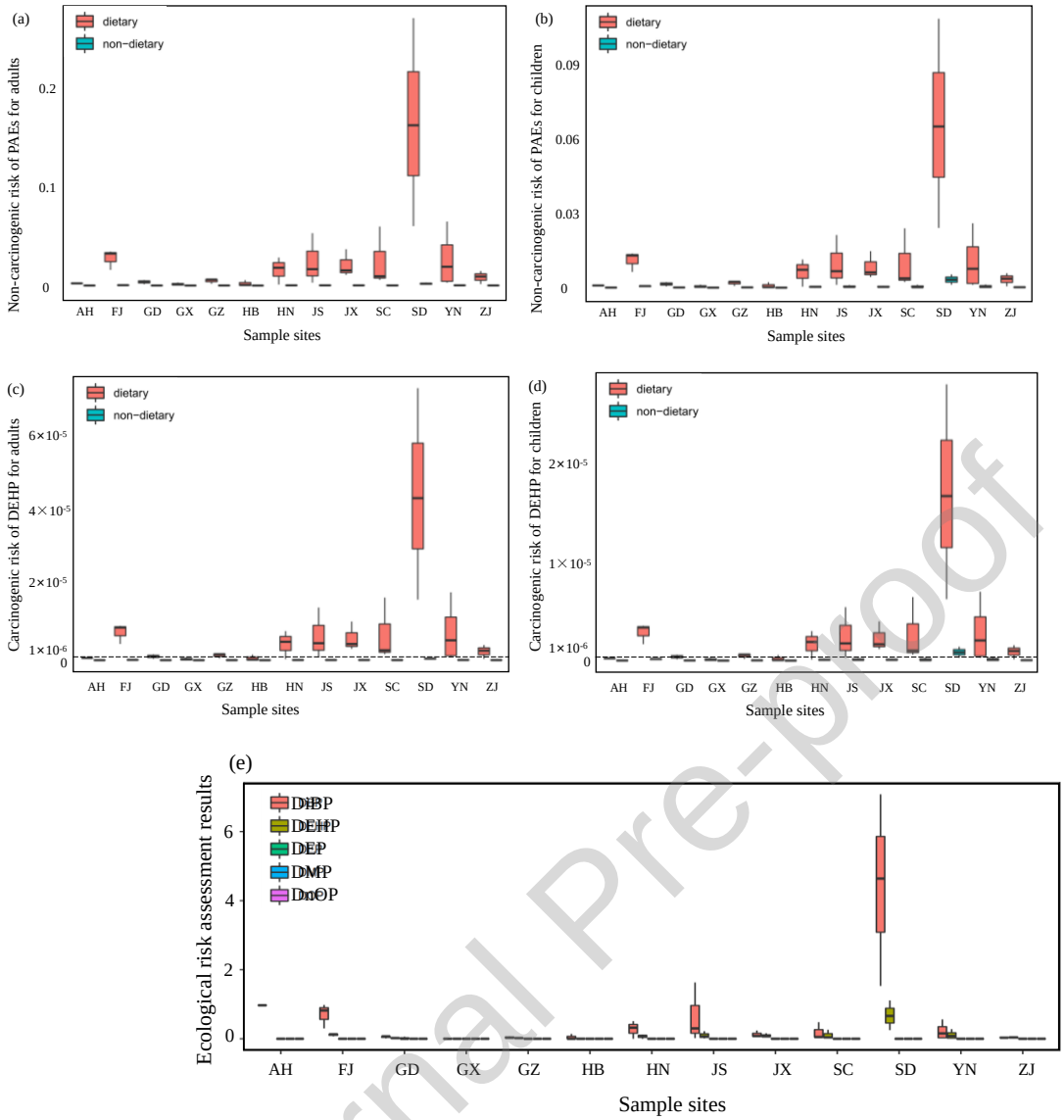


Fig.4 Noncarcinogenic risks of PAEs via non-dietary and dietary routes for adults (a) and children (b), and carcinogenic risks of DEHP via non-dietary and dietary routes for adults (c) and children (d). (e) The ecological risks of PAEs.

Table 1 Concentrations (mg·kg^{-1}) of PAEs in tea plantation soils.

	DMP	DEP	DOP	DiBP	DEHP	∑PAEs
Eastern China (SD, AH, JX, JS, ZJ, FJ)	<0.01	<0.01	<0.01	0.25±0.44a	1.60±2.46a	1.85±2.47a
Central China (HN, HB)	<0.01	ND	<0.01	0.04±0.05b	0.31±0.41c	0.35±0.38c
Southern China (GX,GD)	<0.01	<0.01	<0.01	0.01±0.01b	0.09±0.08b	0.10±0.07c
Southwest China (SC, YN, GZ)	<0.01	ND	<0.01	0.03±0.05b	0.70±0.88b	0.74±0.41b
Maximum	0.00	0.01	0.01	1.56	9.34	10.90
Minimum	ND	ND	ND	ND	ND	0.002
Mean	0.00	0.00	0.00	0.12	0.91	1.03
Standard deviation	0.00	0.00	0.00	0.29	1.69	1.97
Standard error	0.00	0.00	0.00	0.05	0.28	0.33
Skewness	-0.33	5.99	2.55	3.94	3.71	3.77
Kurtosis	-2.00	36.43	5.05	16.36	15.56	15.92

Median	0.00	0.00	0.00	0.01	0.33	0.34
Coefficient of variation	114%	485%	177%	244%	185%	191%

The values of soil samples with different lowercase letters were significantly different from each other ($p < 0.05$); ND: not detected.

Table 2 Concentrations of DEHP and DiBP ($mg \cdot kg^{-1}$) in different types of Chinese agricultural soils.

	DEHP			DiBP			Reference
	Min	Max	Mean	Min	Max	Mean	
Tea plantation	ND	9.34	0.91	ND	1.56	0.12	This Study
Tea plantation	0.71	1.63	1.18	—	—	—	Liao *et al*., 2019
Arable soils	ND	6.22	0.82	0.01	0.34	0.07	Niu *et al*., 2014
Plastic greenhouse	0.24	4.18	1.84	—	—	—	Wang *et al*., 2013
Plastic greenhouse	0.07	5.33	1.46	ND	11.43	1.12	Chai *et al*., 2014
Plastic greenhouse	ND	2.94	0.29	0.10	8.54	1.12	Li *et al*., 2016b
Orchard	0.03	0.10	0.07	—	—	—	Li *et al*., 2015
Paddy field	0.03	0.35	0.11	—	—	—	Li *et al*., 2015
Paddy field	0.08	0.58	0.22	—	—	—	Wang *et al*., 2017
Vegetable field	0.03	0.22	0.14	—	—	—	Wang *et al*., 2017
Vegetable field	0.12	2.54	0.67	ND	3.83	0.64	Zeng *et al*., 2020
Cotton field	ND	1.50	0.10	ND	0.06	0.01	Peng *et al*., 2018
Tobacco field	ND	3.34	0.22	—	—	—	Yu *et al*., 2018
Tobacco field	0.02	0.53	0.23	—	—	—	Song *et al*., 2020
Melon field	ND	0.46	0.05	ND	3.15	0.12	Mahebali *et al*., 2020

"—" indicated lack of data.

Table 3 Correlations of PAEs and soil properties.

	PAEs	DEHP	DiBP	DMP	DEP
DEHP	1.00*				
DiBP	0.98*	0.97*			
DMP	0.08	0.08	0.06		
DEP	-0.07	-0.07	-0.06	0.00	
DOP	-0.24	-0.24	-0.27	-0.25	0.01
pH	0.19	0.18	0.20		
clay	-0.32	-0.32	-0.35		
TOC	-0.24	-0.24	-0.26		
TN	-0.27	-0.27	-0.29		
NH_4^+	0.11	0.11	0.13		
NO_3^-	-0.15	-0.15	-0.17		
P	-0.28	-0.28	-0.25		
S	-0.25	-0.25	-0.27		
Cl	0.08	0.08	0.04		
Si	0.07	0.08	0.05		
Al	-0.16	-0.16	-0.16		
Ca	0.25	0.24	0.28		

Mg	0.13	0.12	0.17
Na	0.66*	0.65*	0.70*
K	0.24	0.23	0.30
Fe	-0.37	-0.37	-0.35

*Significant at 0.05 level (2-tailed)

Table 4 The average values of health risks (mg kg^{-1} day^{-1}) to adults and children from tea plantation soils.

			DMP	DEP	DiBP	DOP	DEHP	PAEs
Health risk								
non-cancer risk (HQ)	Adults	$ADD_{dietary}$	1.35×10^{-7}	6.74×10^{-7}	1.25×10^{-3}	6.72×10^{-5}	2.55×10^{-2}	2.68×10^{-2}
		$ADD_{non\text{-}dietary}$	2.10×10^{-9}	1.05×10^{-8}	1.30×10^{-5}	1.67×10^{-5}	2.58×10^{-4}	2.88×10^{-4}
		ADD_{total}	1.36×10^{-7}	6.81×10^{-7}	1.26×10^{-3}	6.92×10^{-5}	2.57×10^{-2}	2.71×10^{-2}
	Children	$ADD_{dietary}$	5.11×10^{-8}	2.55×10^{-7}	4.74×10^{-4}	1.92×10^{-5}	9.65×10^{-3}	1.01×10^{-2}
		$ADD_{non\text{-}dietary}$	1.82×10^{-9}	9.08×10^{-9}	1.69×10^{-5}	6.82×10^{-7}	4.94×10^{-4}	5.12×10^{-4}
		ADD_{total}	5.29×10^{-8}	2.64×10^{-7}	4.91×10^{-4}	1.99×10^{-5}	1.01×10^{-2}	1.07×10^{-2}
cancer risk (CR)	Adults	$ADD_{dietary}$					7.13×10^{-6}	
		$ADD_{non\text{-}dietary}$					7.22×10^{-8}	
		ADD_{total}					7.20×10^{-6}	
	Children	$ADD_{dietary}$					2.77×10^{-6}	
		$ADD_{non\text{-}dietary}$					1.38×10^{-7}	
		ADD_{total}					2.84×10^{-6}	
Ecological risk								
risk quotient (RQ)			1.28×10^{-4}	2.05×10^{-3}	5.65×10^{-1}	5.49×10^{-6}	2.10×10^{-1}	

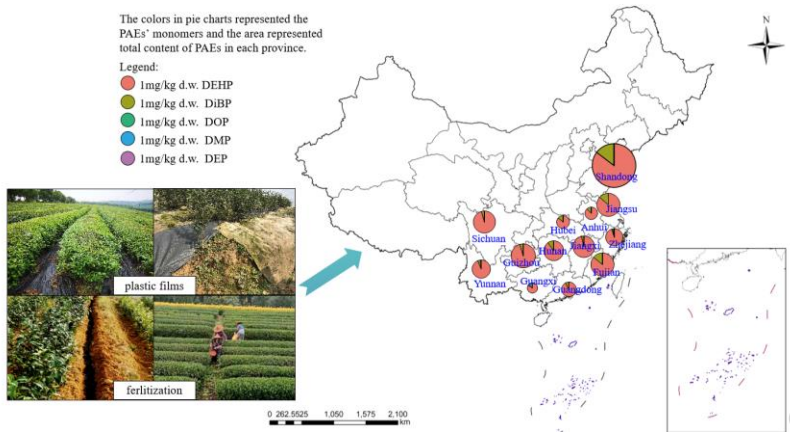
CRediT authorship contribution statement

Yutong Li: Formal analysis, Visualization, Data Curationt, Writing - Original Draft. **Jun Wang**: Funding acquisition, Project administration, Writing - Review & Editing. **Hongcheng Bai**: Investigation, Writing - Review & Editing. **Kang Ni**: Investigation, Data curation. **Kun Liu**: Investigation, Data curation. **Peili Lu**: Writing - Review & Editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Graphical abstract



Highlights

- DEHP was the major congener in tea plantation soils, posing potential cancer risks.
- The highest ∑PAEs content in tea plantation soil was observed in Shandong Province.
- The potential sources of PAEs could be plastic films and fertilizers primarily.