



# Phthalate esters in biota, air and water in an agricultural area of western China, with emphasis on bioaccumulation and human exposure

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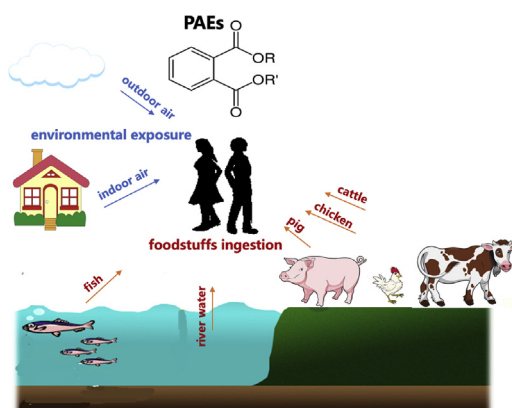
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## HIGHLIGHTS

- Composition profiles of PAEs in biota differed from those in ambient environment.
- Significant correlations were obtained between the biota and river water samples.
- Most PAEs congeners are not likely to be accumulative in organisms.
- River water intake was the major contributor for human exposure to PAEs.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Phthalate esters (PAEs) have been shown to be ubiquitous in abiotic and biotic environmental compartments; however, information about bioaccumulation behavior and human exposure, both via environmental exposure and the diet, are limited. Herein, we report the concentrations and composition profiles of phthalate esters (PAEs) in biological samples, river water, indoor air, and outdoor air samples collected from an agricultural site in western China. Dibutyl phthalate (DNBP) occupied a relatively high abundance in biological samples, discrepant with the environmental samples in which di-(2-ethylhexyl) phthalate (DEHP) was the dominant congener. Significant correlations ( $P < 0.05$ ) were observed between the biota and river water samples, indicating that river water heavily influenced PAE accumulation in biological samples. The mean log Bioaccumulation Factors (BAFs) varied from 0.91 to 2.96, which implies that most PAE congeners are not likely to accumulate in organisms. No obvious trends were observed between log octanol-water partition coefficient ( $K_{OW}$ ) and log BAF values, nor between log octanol-air partition coefficient ( $K_{OA}$ ) and biota-air accumulation factors (BAAFs). Nevertheless, the calculated log air-water partitioning factors (AWPFs) of diethyl phthalate (DEP), dimethyl phthalate (DMP), and butyl benzyl phthalate (BBP) were similar to predicted values whereas those for diisobutyl phthalate

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(DIBP), DNBP and DEHP were significantly higher. The estimated daily intakes of PAEs via food ingestion and environmental exposure were 15, 9.4 and 1.2 ng/kg-bw/day in toddlers, children and adults, respectively, laying at the low end of the reported data and well below the reference dose.

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## 1. Introduction

Phthalate esters (PAEs) are ubiquitous environmental contaminants worldwide due to their extensive use as plasticizers in a variety of products, including polyvinylchloride (PVC) resins, construction materials, food packaging, personal care products, cosmetics, and electronic equipment (Wittassek et al., 2011; Dominguez-Morueco et al., 2014). Since PAEs are not chemically bound to the products, they tend to migrate into the environment during disposal of PAE-containing products. As a result, the widespread use of PAEs in our daily life has led to their notorious presence in various environmental matrices such as soil, water, air, dust, biota, and human tissues, as described in recent reviews (Gao et al., 2018; Net et al., 2015). The global production of PAEs increased from 2.7 to approximately 6 million tons per year from 2007 to 2017 (Gao et al., 2018). Currently, China has become the largest PAE importer in the world, with its domestic demand for PAEs increasing at a rate of 7.7% from 2010 to 2015 annually (Zhang et al., 2015).

There is increasing evidence that PAEs pose hazards to both aquatic and terrestrial organisms, including humans (Staples et al., 1997). For example, butyl benzyl phthalate (BBP), dibutyl phthalate (DNBP) and di-(2-ethylhexyl) phthalate (DEHP) can cause estrogenic disruption in zebrafish embryo (Chen et al., 2014). PAEs can also result in reproductive, hepatic and renal problems in humans exposed to PAEs after long-term exposure (Hauser and Calafat, 2005; Swan, 2008; Liu et al., 2012). To this end, restrictive regulations have been issued to curb the use of PAEs. For instance, six PAE congeners have been listed as priority pollutants by the US Environmental Protection Agency (Net et al., 2015) and the Council of the Europe Union has implemented regulations to restrict the use of PAEs in toys and childcare articles (EU, 2005).

The log octanol-water partition coefficient ( $K_{ow}$ ) values of PAEs ranges from 1.61 to 12.06 (Net et al., 2015). While PAEs with high  $K_{ow}$  values are expected to accumulate in organisms, only a few published studies have focused on PAE occurrence in biota, and most of them were associated with aquatic systems. The publications that studied PAE concentrations in fish and marine mammals reported PAE concentrations up to several  $\mu\text{g/g}$  wet weight (Cheng et al., 2013; Huang et al., 2008; Güven and Coban, 2013; Fossi et al., 2012). Bioaccumulation and bioconcentration factors (BAFs and BCFs) are employed to illustrate the tendency of chemicals to accumulate in specific organisms, and values that larger than 1000 may indicate high accumulation potential (Net et al., 2015). Only a few BAF/BCF values for PAEs have been reported so far and considerable differences exist among published values. For instance, relatively low BCF values for certain PAEs were reported for mammals and invertebrates, with values varying from 0.0024 to 0.24 (Net et al., 2015); however, BCFs ranging from 120 to 9300 were reported for five species of fish in other study (Net et al., 2015). The wide range of BAF/BCF values has been ascribed to the different metabolic rates of individual PAEs in different organisms (Net et al., 2015). In addition, the levels and composition of PAEs in the environmental matrices where the organisms live may heavily influence bioaccumulation behavior. A recent study reported that both the metabolic rates and the PAE profile in the environment in which an organism lives heavily influences the PAE profile found in the organism (Adegun et al., 2015).

For humans, both environmental exposure and food intake are potential pathways for PAE accumulation (Guo and Kannan, 2011; Koniecki et al., 2011). Several studies have investigated human exposure to PAEs via air, dust, food, and drinking water in urban areas with high population density (Das et al., 2014; Weschler, 2003; Zhang

et al., 2014; Ji et al., 2014). Das et al. (2014) determined that food intake was the major source of PAE exposure for humans, contributing >67% of the exposure. On the other hand, Ji et al. (2014) found that food intake and environmental exposure contributed equally to human exposure to PAEs. Therefore, human exposure pathways may vary in regions with different PAE sources. To date, human PAE exposure and bioaccumulation via food intake and environmental exposure has not been reported in rural areas with no specific PAE sources.

To address the lack of information about PAE exposure to humans in rural areas, we conducted a comprehensive investigation into biotic (domestic livestock, fish, vegetables), indoor and outdoor air, and river water samples collected from an agricultural area of western China. Our objectives were to compare the concentrations and congener profiles in various matrices, calculate bioaccumulation factors for PAEs, and estimate the exposure dose for humans via both diet and environmental exposure. This study may provide a comprehensive understanding of human exposure to PAEs via both exposure routes.

## 2. Materials and methods

### 2.1. Chemicals and materials

An analytical standard containing 1000 mg/L each of seven individual PAEs, including diethyl phthalate (DEP), dimethyl phthalate (DMP), BBP, DNBP, diisobutyl phthalate (DIBP), di-n-octyl phthalate (DNOP), and DEHP, was obtained from o2si smart solutions (USA). DEP- $d_4$ , DMP- $d_6$ , DNBP- $d_4$ , and DEHP- $d_4$  were purchased from Dr. Ehrenstorfer GmbH (Germany) for use as internal standards. Acetone, n-hexane, and ethyl acetate (high performance liquid chromatography (HPLC) grade) were purchased from J. T. Baker (USA) and dichloromethane was obtained from Adamas (China). Methanol and acetonitrile (HPLC mass spectrometry) grade were obtained from Merck (Germany). Cleanert Florisil Solid Phase Extraction (SPE) columns (6 mL/1000 mg) were obtained from Agela technologies (China).  $C_{18}$  SPE columns were obtained from Agilent (USA).

### 2.2. Sample collection

All samples were collected in an agricultural area of Chongqing, Wanzhou County, China (Fig. 1) as part of the same study described previously by He et al. (2019). The Yangtze River flows through Wanzhou County and is the water source for human drinking and irrigation. Fig. 1 shows the specific locations for biota, river water, and air sample collection sites. All biotic and water samples were collected on the same day in July 2017. Indoor air samples were collected during June 2017 whereas outdoor air samples were collected from June to September 2017.

Muscle tissue samples from domestic livestock (7 pigs, 7 cattle, and 7 chickens) that had been raised on the farm for more than one year. One species of fish, the Crucian carp (*Carassius carassius*), ( $n = 7$ ) was collected in the Yangtze River using fyke nets fitted with otter boards. After dissection, muscle tissue samples (~50 g) were wrapped with aluminum foil. Vegetables, including Chinese chives ( $n = 2$  plants), potatoes ( $n = 2$ ), cabbages ( $n = 2$ ), and carrots ( $n = 2$ ), were collected near the farm.

Low-volume air samplers (TH-3150, TianHong, China) were used to collect indoor and outdoor air samples. Gas-phase PAEs were collected with pre-cleaned polyurethane foam (PUF) (50-mm diameter  $\times$  15-



Fig. 1. Location of the sampling site.

mm thick) plugs. Samples were collected every other day for one month so that 15 samples were collected at each site. Samplers were operated at a flow rate of 5 L/min and samplers ran for 24 h per day, thus 7.2 m<sup>3</sup> of air was drawn through the sampler each day and 108 m<sup>3</sup> of air was collected at each site. PUF plugs were extracted separately and then the 15 extracts from each site were combined so that one combined extract was analyzed per site. This approach was used to obtain enough mass of PAEs per site for quantification.

One sampler was rotated between three different resident's houses located near the farm and a sample was collected every other day during June 2017. Two outdoor air samplers were rotated between seven different sites located with an area of 5 km<sup>2</sup> surrounding the farm, with samples being collected every other day from July through September 2017. One indoor and one outdoor field blank (pre-cleaned PUF plugs) were also transported to the sampling area, mounted in the sampler, dismounted, collected, and analyzed concurrently with the samples.

A total of 14 river water samples were collected on a single day in July 2017 from the Yangtze River at the sites shown in Fig. 1. The water samples were collected at 30–40 cm below the surface and stored in pre-cleaned glass containers (2.5 L). Approximately 10 L of water was collected for each sample and then transported to the laboratory immediately and analyzed within 24 h.

### 2.3. Sample preparation and instrumental analysis

All biota samples were freeze-dried and ground into powder. PAEs were extracted from ~1 g of animal tissue and ~5 g of vegetable powders with Soxhlet for 24 h using a mixture of acetone/n-hexane (1:1, v/v). A known amount of internal standards was spiked into sample powers before extraction. An aliquot of the extract (1:10, v/v) was used for lipid analysis, which was conducted gravimetrically. The remaining extract was used for PAE analysis and the purification procedure was the same as with PUF.

PAEs were extracted from the PUF discs used for air sampling with Soxhlet extraction using a mixture of acetone/n-hexane (1:1, v/v) for 24 h. Prior to extraction, PUF discs were spiked with known amounts of the internal standards listed above. Extracts were concentrated and

solvent exchanged to hexane. Extracts were then purified using Florisil SPE columns that had been pre-cleaned with 6 mL hexane and 6 mL ethyl acetate. After loading the extracts in columns, PAEs were eluted with 15 mL ethyl acetate, solvent exchanged to hexane, and then evaporated to dryness under a gentle nitrogen stream. Finally, the residue was dissolved in 200 µL of methanol.

Water samples (~0.5 L) were filtered with glass fiber filters (47-mm diameter) (Whatman, England), spiked with internal standards, and then flowed through a C<sub>18</sub> SPE column that had been pre-activated with 5 mL ethyl acetate, 5 mL methanol and 5 mL ultrapure water. Then the column was vacuum dried and PAEs were eluted with 15 mL ethyl acetate. Extracts were then solvent exchanged to hexane, evaporated to dryness, and then the residue was dissolved in 200 µL of methanol.

PAEs were quantified with an Ultra Performance Liquid Chromatography (UPLC) system coupled to a Quadrupole Time of Flight Mass Spectrometer (TOF-MS) (Waters, Xevo G2, USA) using a method described previously (He et al., 2018). An ACQUITY BEH C<sub>18</sub> column (100 mm length × 2.1 mm i.d., with 1.7 µm diameter particles) (Waters, USA) was used to achieve the chromatographic separation. Mobile phase A was Milli-Q water containing 0.1% formic acid and mobile phase B was acetonitrile. The gradient program was 0–0.5 min, 40% B; 0.5–3.0 min, 50% B; 3–4.5 min, 55% B; 4.5–8.5 min, 70% B; 8.5–9 min, 100% B; 9–13.8 min, 100% B; 13.9–16 min, 40% B. Mass Spectrometry Elevated (MSE) mode, with positive electrospray (ESI), was employed and the quantification ions for all PAEs were [M + Na]<sup>+</sup>. All data were processed using MassLynxTM4.1 software (Waters, USA).

### 2.4. Quality assurance

Matrix effects were evaluated by spiking known amounts of target PAEs (100 ng) and internal standards (200 ng) into a pooled sample composed of animal tissues and a river sample. The recoveries of spiked PAEs in animal tissue and water samples, calculated on peak areas, varied from 60% ± 13% (% relative standard deviation, %RSD) to 120% ± 11%, and from 76% ± 9% to 122% ± 4% among different PAE congeners, respectively. In addition, method precision was measured by analyzing Milli-Q water that had been spiked with target PAEs, at two

concentrations (100 ng and 1000 ng), and internal standards. The %RSD of recoveries of target PAEs and internal standards were <15% (Table S1 in the Supplementary material).

To minimize the potential contamination of samples with potential sources of PAEs from the laboratory, all glassware was solvent rinsed and baked at 450 °C prior to use. Procedural blanks, that underwent all sample preparation steps, were processed with each batch of ten samples. Only DNBP (164 ± 21 ng/mL) and DEHP (54 ± 19 ng/mL) were detected in procedural blanks and these concentrations were subtracted from measured concentrations in samples from the same batch. The recoveries of internal standards in the procedural blanks and samples ranged from 77% to 94% and from 73% to 95%, respectively. The limit of quantification (LOQ) and the limit of detection (LOD) for each PAE congener are provided in Table S1. For most congeners, the LOD and LOQ were defined as the concentrations at which the peak areas were 10:1 and 3:1. For DNBP and DEHP, which were detected in the procedural blanks, the LOD and LOQ were defined as the mean concentration in blanks plus ten times or three times the standard deviation of blanks, respectively.

### 3. Results and discussion

#### 3.1. Concentrations and relative abundances of PAEs in biotic samples

The mean, median and range of concentrations measured for individual PAE congeners, and for the sum of all measured congeners (ΣPAE), in each type of biotic sample (pig, chicken, cattle, fish, and vegetables) are presented in Table 1. With the exception of DNOP, all PAE congeners were detected in every sample type, which demonstrates the ubiquity of PAEs in this study area. The pig samples had the highest ΣPAE concentrations (51.3 ± 3.6 ng/g dry weight (dw)) (mean value ± standard deviation), followed by fish (49.2 ± 9.9 ng/g dw), chicken (44.8 ± 4.6 ng/g dw) and cattle samples (30.7 ± 1.2 ng/g dw).

The percent lipid content was 9.45% ± 2.86% in pig, 7.22% ± 1.71% in fish, 6.96% ± 1.53% in chicken, and 4.59% ± 1.05% in cattle samples. The lipid content was not measured for vegetables. Correlation analysis revealed a significantly positive relationship ( $P < 0.05$ ) between the ΣPAE concentration and percent lipid (Fig. 2), indicating that animals with higher lipid content accumulated more PAEs. Of note, the highest concentrations of DEHP and DNOP were higher in fish and chicken than pig (Table 1) even though their lipid contents were lower than in the pig samples. For DEHP, this was likely due to the variations in metabolic rates of DEHP in different organisms (Hu et al., 2016; Fossi et al., 2012; Net et al., 2015). A number of past studies have also shown that the lipid content in biological samples can significantly affect the accumulation of hydrophobic organic pollutants. For example, this was true for brominated flame retardants and polychlorinated biphenyls in North sea food web (Boon et al., 2002), polybrominated flame retardants in Baltic sea food web (Bureau et al., 2006), and polycyclic

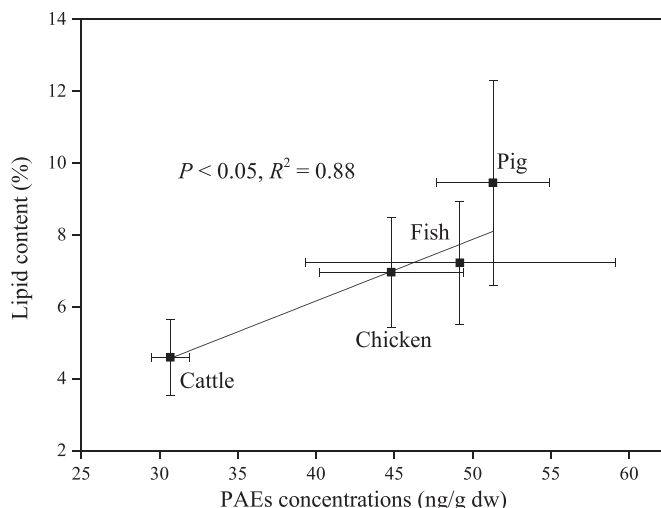


Fig. 2. Correlation between PAEs concentrations and lipid content. Error bars indicate standard deviation.

aromatic hydrocarbons in most milk and meat samples (Santonicola et al., 2017). However, we did not observe a significantly positive relationship for some organophosphate esters in the same animal tissue samples collected at our site and reported previously, and this relationship has not previously been reported for PAEs.

The mean ΣPAE concentration in fish tissue from this study (49.2 ± 9.9 ng/g dw) (Table 1) was comparable to sum of detected PAEs reported in False Creek in Vancouver, Canada (Lin et al., 2003), but several orders of magnitude lower than those reported for fish in Hong-Kong (Cheng et al., 2013), Nigeria (Adeniyi et al., 2011), Seine River and Orge River, France (Teil et al., 2014) and Taiwan (Huang et al., 2008). There is not enough previously reported data for PAEs in animal tissues to make similar comparisons for pig or chicken.

DNBP was the predominant PAE congener measured in each type of animal tissue (Fig. 3), with a relative abundance of 56.8%, 56.0%, 49.7%, 67.3% in fish, pig, chicken and cattle, respectively. DNBP was also the dominant PAE congener in fish samples from other studies (Cheng et al., 2013; Adeniyi et al., 2011; Lin et al., 2003). It is worth noting that the relative abundance of DEHP in chicken (33.4%) was higher than that found in other animals. Higher abundance of DEHP was also confirmed by some studies where DEHP exhibited an equivalent abundance to DNBP (Hu et al., 2016; Huang et al., 2008; Mackintosh et al., 2004). One likely reason was attributed to the species-dependent of PAEs distribution in organisms, which was the possible result of the combination between bioaccumulation and metabolism in the organisms (Hu et al., 2016; Net et al., 2015). Apart from that, the influence of the environmental matrices on the PAEs distribution in the organism should not be ruled out (Hu et al., 2016).

Table 1 Concentrations (ng/g dry weight) of PAEs in biotic samples.

	Fish (n = 7)			Pig (n = 7)			Chicken (n = 7)			Cattle (n = 7)			Vegetables (n = 8)		
	Mean	Median	Range	Mean	Median	Range	Mean	Median	Range	Mean	Median	Range	Mean	Median	Range
DMP	3.24	3.23	2.66–3.67	4.83	4.83	4.18–5.96	3.53	3.56	3.36–3.68	3.67	3.65	3.53–3.82	28.8	28.4	21.0–38.4
DEP	1.10	1.00	0.57–1.64	6.08	3.18	1.80–16.7	0.77	0.67	0.33–1.44	0.48	0.46	0.35–0.81	18.4	7.90	2.42–69.1
BBP	0.45	0.25	0.12–1.19	0.85	0.82	0.41–1.16	0.27	0.28	0.17–0.42	0.52	0.64	0.17–0.92	1.24	1.17	1.03–1.68
DIBP	2.16	2.14	2.00–2.40	7.14	6.93	4.20–12.9	2.31	2.10	1.30–3.73	2.01	1.96	1.57–2.36	32.0	27.3	0.63–77.8
DNBP	25.9	23.2	21.0–44.5	28.3	27.4	26.4–34.0	21.1	21.9	17.9–24.7	20.5	20.3	19.6–22.3	213	192	155–338
DEHP	16.3	10.2	2.05–52.5	4.08	3.07	1.00–9.09	16.6	16.7	1.83–30.5	3.43	5.16	nd–6.78	36.4	33.8	12.6–75.9
DNOP	0.09	0.13	nd–0.22	0.06	na	nd–0.13	0.14	0.14	0.13–0.15	0.07	0.13	nd–0.14	0.79	1.19	nd–1.37
ΣPAEs	49.2	38.8	30.0–105	51.3	50.1	43.2–70.9	44.8	50.0	27.0–59.0	30.7	32.6	26.9–34.4	330	278	248–532

nd-not detected.

na-not calculated because there was only one detection.

For statistical calculations (mean and median), non-detects were replaced with the LOQ value.

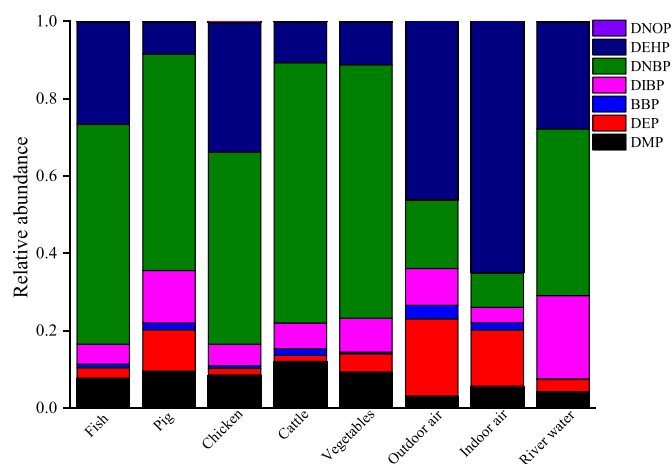


Fig. 3. Mean PAE profile in biota and environmental samples.

The  $\Sigma$ PAE concentration in vegetables varied from 248 to 532 ng/dw, markedly lower than those reported in other studies (Wang et al., 2015; Wu et al., 2013). DNBP was the predominating compound in vegetables, responsible for 65.6% of the total PAEs, while Wang et al. (2015) reported the abundance of DNBP varying due to the different types of vegetables. Wu et al. (2013) also found that leaf vegetables have a higher ability absorbing DEHP from the air compared to stem vegetables. In this study, most of the vegetables were stem vegetable, and therefore this may be the reason for the lower abundance of DEHP (10.9%).

### 3.2. Concentrations and relative abundances of PAEs in air and water

The mean, median and range of concentrations measured for individual PAE congeners, and for the sum of all measured congeners ( $\Sigma$ PAE), are shown in Table 2. The mean  $\Sigma$ PAE concentration in indoor air ( $2820 \pm 222$  pg/m<sup>3</sup>) was similar to that in outdoor air ( $3030 \pm 320$  pg/m<sup>3</sup>). In contrast, several other publications have reported higher PAE concentrations in indoor compared to outdoor air due to the extensive use of products containing phthalates in the indoor environment (Chen et al., 2018; Wang et al., 2014). The difference may be due to the homes in this study containing simple furniture and few electronic appliances. The PAE concentrations in both indoor and outdoor air in this study were up to several orders of magnitude lower than those measured in Beijing (125 to 498 ng/m<sup>3</sup>) (Chen et al., 2018), Shanghai (5.7 to 8.0 ng/m<sup>3</sup>) (Ma et al., 2014), Tianjin (1.3 to 19.4 ng/m<sup>3</sup>) (Zhu et al., 2016; Kong et al., 2013), Nanjing, China (3.1 to 10 ng/m<sup>3</sup>) (Wang et al., 2008), Paris (1.9 ng/m<sup>3</sup>) (Teil et al., 2006) and Greece (from 1.1 to 2.0 ng/m<sup>3</sup>) (Salapidou et al., 2011). Again, this was likely due to the rural nature, and relatively low use of PAE-containing products, at our site.

DEHP was the predominant PAE congener in air samples, with an average relative abundance of 46.3% and 65.6% in outdoor and indoor air, respectively (Fig. 3). This is in contrast to our observation for biota samples where DNBP was the dominant congener. In several previous studies, DEHP was also the dominant congener in air samples (Song et al., 2015; Kong et al., 2013; Blanchard et al., 2014; Tran et al., 2017; Mandin et al., 2016; Teil et al., 2006); however, PAE profiles containing a dominant DNBP abundance in air have also been reported (Chen et al., 2018; Zhang et al., 2014; Tran et al., 2017). DEHP and DNBP are the primary plasticizers applied and produced in China (Wang et al., 2010; Zhang et al., 2015) thus it is interesting that the abundance of DEHP is so much higher than that of DNBP at our site. This observation may be largely due to the variability in the types of PAE-containing products used in different parts of the country. For instance, DNBP is widely used in latex adhesives and personal care products, which may not be used extensively in rural Wanzhou County, whereas DEHP is widely used in PVC plastics, building products and food packaging (Heudorf et al., 2007; Abb et al., 2009).

The PAEs levels in river water varied from 364 to 1300 ng/L, with a mean value of  $599 \pm 69$  ng/L (Table 2). No statistical differences were obtained among the 14 sampling sites (ANOVA). All the PAEs compounds were detected in the river water suggesting PAEs were ubiquitous in the river system. So far, numerous studies have reported the occurrence of PAEs in river water which were well documented in recent reviews (Net et al., 2015; Zhang et al., 2015). In contrast to some studies conducted in different parts of the Yangtze River, the PAEs levels in the present study were comparable to those from Jiangsu (from 178 to 1474 ng/L) (He et al., 2011), but one order of magnitude lower than those from Wuhan (from 34 to 91,220 ng/L) (Wang et al., 2008) and Yangtze River Delta (61 to 28,550 ng/L) (Zhang et al., 2012). The Yangtze River collected in this study passes through the Three Gorges Reservoir Region which located in a remote area, so the influence of anthropogenic activities should be considered to some limited extent. In terms of the PAE profiles, the river water was mostly characterized by DNBP, DEHP, and DIBP, with a mean abundance of 43.1%, 27.7% and 21.5%. It is reported that DIBP/DNBP with low molecular weight, are commonly used in cosmetics and personal care products (Huo et al., 2016), thus they may be likely originated from the upstream of the Yangtze River during fluid transport.

### 3.3. Role of ambient environments as sources of PAEs in biota

Previous studies have revealed that the metabolic capacity of the species as well as the ambient environment (feeding habits) were the vital factors to the PAEs distribution in biota (Adeogun et al., 2015). It is obvious to note that the biota exhibited discrepant PAEs composition profiles from the outdoor air and water samples where DNBP predominated in biota while DEHP was the major compound in air and water samples. It is demonstrated that PAEs could degrade in the environment and the degradation rate differs among the PAEs compounds under varying redox-conditions (Chang et al., 2005; Roslev et al., 2007; Yuan

Table 2  
Mean, median and range of PAE concentrations in air and river water samples.

	Outdoor air (pg/m <sup>3</sup> )			Indoor air (pg/m <sup>3</sup> )			River water (ng/L)		
	Mean	Median	Range	Mean	Median	Range	Mean	Median	Range
DMP	85.5	74.3	64.6–126	159	167	135–176	23.2	22.8	16.7–37.4
DEP	605	554	400–966	397	345	297–549	18.3	14.8	8.63–57.4
BBP	86.0	110	Nd–209	53.2	62.6	32.4–64.7	0.88	0.85	0.53–1.35
DIBP	287	217	172–708	110	90.4	90.1–152	120	110	77.4–205
DNBP	522	527	319–666	252	274	146–334	277	201	135–801
DEHP	1440	1400	713–2600	1850	1690	1550–2300	159	149	73.3–261
DNOP	nd	na	na	nd	na	na	0.69	0.72	0.50–1.06
$\Sigma$ PAEs	3030	2970	2150–4570	2820	2710	2500–3250	599	524	364–1300

nd-not detected.  
na-not available.

et al., 2002), and DEHP with long and complex side chains was proved to have a higher half-life than DNBP shorter alkyl-side chains in a variety of environments (Zhao et al., 2017), resulting in the persistency of DEHP in the environmental matrices. Interestingly, elevated DNBP concentrations rather than DEHP were measured in biota, which could be interpreted by the fact that the organisms tend to accumulate PAEs with lower molecular weight and shorter alkyl-side chains like DNBP rather than higher molecular weight and long chains like DEHP (Adeogun et al., 2015; Song et al., 2019). Nevertheless, PAE profiles dominating by DEHP both in fish and sediment were observed in a study by Huang et al. (2008) where the biota-sediment accumulation factor (BSAF) of DEHP was larger than 1, signifying that the organism can accumulate DEHP from the environment matrix. Thus, the PAE distribution in biota was influenced by a variety of complex factors including metabolic capacity of the organisms as well as the ambient environment.

To further investigate the impact of ambient environment on the PAE distribution in biota, we analyzed the correlation between PAEs in biota and ambient environmental samples based on the logarithmic transformation. As can be seen in Table 3, significant correlations were obtained between the biota and water samples, suggesting that river water heavily impacted the PAE accumulation in biological samples. As expected, the river water was the main water source for the biota and irrigation for vegetables in this area. On the contrary, weak correlations were showed between the air and the biota, even for the terrestrial biota, which demonstrated that river water as a diet exposure should be considered as a primary pathway for PAE accumulation in biota rather than the environmental exposure to air in this studying area.

### 3.4. Bioaccumulation behavior of PAEs

The bioaccumulation factors (BAFs), biota-air accumulation factors (BAAFs), as well as the air-water partitioning factors (AWPFs) were calculated according to the formulas presented below:

$$\text{BAFs} = 10^6 \times \frac{C_{\text{biota}}}{C_{\text{water}}} \quad (1)$$

$$\text{BAAFs} = 10^6 \times \frac{C_{\text{biota}}}{C_{\text{air}}} \quad (2)$$

$$\text{WAPFs} = 10^3 \times \frac{C_{\text{water}}}{C_{\text{air}}} \quad (3)$$

where  $C_{\text{biota}}$  is the mean concentration of in biota (ng/g dw),  $C_{\text{water}}$  is the mean concentration of PAEs congeners throughout all 14 sites in river water (pg/L) and  $C_{\text{air}}$  is the mean concentration of PAEs congeners in outdoor air (pg/m<sup>3</sup>) (Guo et al., 2017).

Previous studies indicated that species could obtain a high capacity for accumulating the pollutant when the BAFs values were larger than 1000 ( $\log(\text{BAFs}) > 3$ ) (Net et al., 2015). In this study, the mean  $\log(\text{BAFs})$  values varied from 0.91 to 2.96, which may imply that most PAEs congeners are not likely to be accumulative in organisms. BAFs values of individual PAEs with large variances can also be found in

other studies (Net et al., 2015), and this could be explained based on the discrepant physicochemical properties of individual PAEs, variances in temporal bioavailability, and species-specific in metabolic capability, resulting in individually and/or jointly impacting on the bioaccumulation of PAEs in the biota (Adeogun et al., 2015). In addition, we plotted the  $\log(\text{BAFs})$  values as a function of the  $\log(K_{\text{OW}})$  values, and  $\log(\text{BAAFs})$  values as a function of the  $\log(K_{\text{OA}})$  values which were presented in Fig. 4. No obvious trend was observed between  $\log(K_{\text{OW}})$  and  $\log(\text{BAFs})$ . DEP, DMP and BBP were elevating along with the increasing  $\log(K_{\text{OW}})$  values, however DNBP, DIBP, DEHP and DNOP deviated this trend, likely due to fast degradation and metabolism inside living organisms (Fig. 4a) (Hu et al., 2016). As shown in Fig. 4b, no linear relationship was exhibited between  $\log K_{\text{OA}}$  and  $\log(\text{BAAFs})$  values, but with the  $\log K_{\text{OA}}$  increasing, a slightly descending tendency was showed with DNBP/DIBP deviated this trend. However, this observation was inconsistent with our previous study on OPEs where the  $\log(\text{BAAFs})$  values of individual OPEs exhibited an increasing tendency with the  $\log K_{\text{OA}}$  ascending (He et al., 2019). In general, one likely explanation for this may be ascribed to the fast metabolism of PAE compounds in organisms (Hu et al., 2016). On the other hand, the different gas-particle partitioning behaviors between OPEs and PAEs may be another key factor for this observation. Past studies revealed that OPEs were primarily partitioned to particles in the atmosphere (Salamova et al., 2014; Möller et al., 2011), while PAE compounds showed various partitioning patterns. For example, DEP, DMP and DNBP/DIBP were reported to be predominantly in gas phase, while BBP and DEHP/DNOP were mainly existent in particle phase (Xie et al., 2007). Moreover, we also compared the relationship between the calculated  $\log(\text{AWPFs})$  and the predicted values. Apparently, the calculated  $\log(\text{AWPFs})$  values of DEP (−5.01), DMP (−5.40) and BBP (−4.08) were rather similar with the predicted values (DEP: −4.48, DMP: −5.43, BBP: −4.01), suggested that the equilibrium state of these compounds between the air and river water was achieved. Nevertheless, the calculated  $\log(\text{AWPFs})$  values for DIBP (−5.62), DNBP (−5.72) and DEHP (−5.04) were significantly higher than the predicted values (DNBP/DIBP: −4.27, DEHP: −2.8), probably due to the continuous input of these predominating PAEs compounds in this area, so that the equilibrium state between the air and water was not obtained.

### 3.5. Human exposure assessment

The DI values of PAEs via both dietary intake and environmental exposure were estimated using the equations and parameters provided in Tables S2 and S3. As shown in Table 4, the DIs of PAEs via food ingestion and environmental exposure were 15, 9.4 and 1.2 ng/kg-bw/day in toddlers, children and adults, respectively. The DIs of DNBP were the highest, followed by DEHP via both food and river water intakes, while the DIs of DEHP were highest in indoor and outdoor air. The percentage contribution via food intake, river water, outdoor air and indoor air to the DIs was shown in Fig. S1. River water was the major source of exposure, responsible for 79%, 83% and 88% of the estimated DIs in toddlers, children and adults, respectively, which exhibited a increasing trend with age, and this was in agreement with another study by Ji et al. (2014). Apart from the river water, food intakes have contributed approximately 15%, 8% and 5% in toddlers, children and adults, respectively, showing a descending tendency. Earlier studies have revealed that dietary exposure is the primary exposure pathway for PAEs (Clark et al., 2011; Das et al., 2014; Ji et al., 2014), and the contribution from the drinking water should be negligible (Das et al., 2014). However, water intake was the main contributors in this study, mainly due to the fact that the river water instead of the tap water was the dominating source for the human intake in this remote area.

Compared with other studies based on various approaches, the estimated DI values in this study were one or two orders of magnitude lower than those reported in Tianjin, China via detecting the concentrations in media (761.8 ng/kg-bw/day for toddlers, 587.5 ng/kg-bw/day

**Table 3**  
Pearson correlation analysis between biological samples and the ambient environments.

	VS water			VS air		
	r	P value	R <sup>2</sup>	r	P value	R <sup>2</sup>
Fish	0.933	0.002	0.870	0.573	0.179	0.328
Pig	0.856	0.014	0.734	0.162	0.728	0.026
Chicken	0.918	0.003	0.844	0.653	0.111	0.427
Cattle	0.862	0.013	0.742	0.165	0.723	0.027
Vegetable	0.882	0.009	0.778	0.195	0.675	0.038

r, Pearson coefficient.

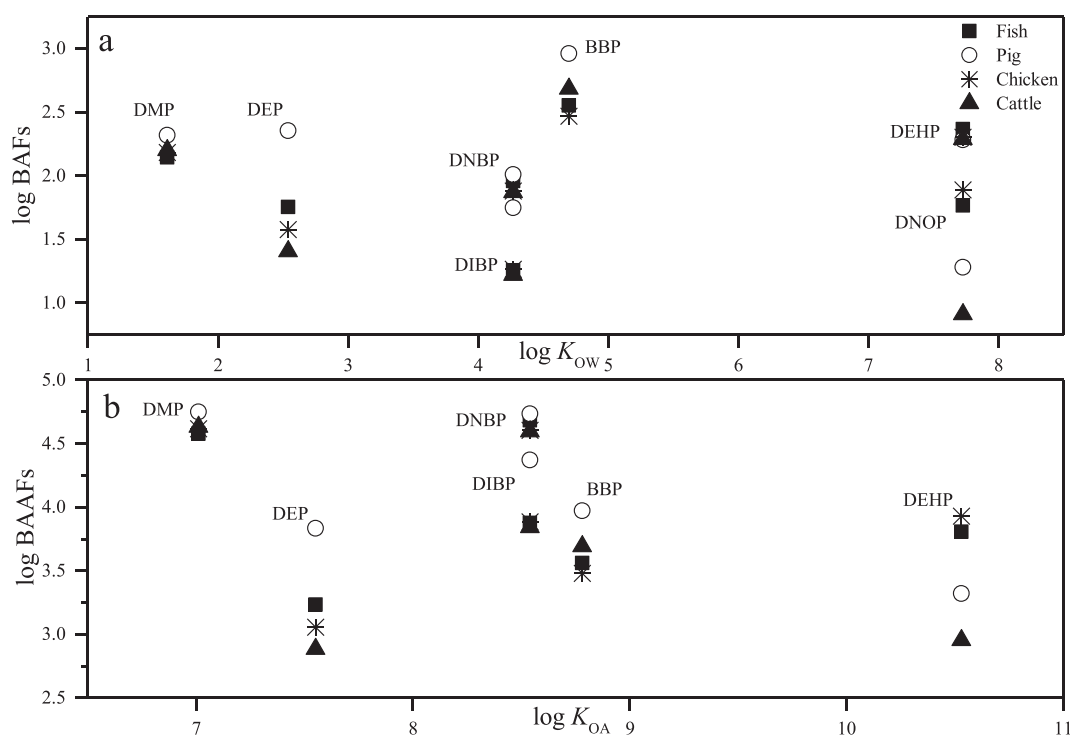


Fig. 4. Correlation between log BAFs and  $\log K_{ow}$ .

for children, 574.0 for adults) (Ji et al., 2014), orders of magnitude lower than those found in South Delhi via detecting the concentrations in media (from 121 to 388  $\mu\text{g}/\text{kg}\text{-bw}/\text{day}$ ) (Das et al., 2014), and well lower than those studies in USA (varied from 15.1 to 75.9  $\mu\text{g}/\text{kg}\text{-bw}/\text{day}$ ) (David, 2000; Kohn et al., 2000), Japan (4.4  $\mu\text{g}/\text{kg}\text{-bw}/\text{day}$ ) (Itoh et al., 2007) via calculating from urinary metabolite. Generally, the large variations of estimates DIs for PAEs may be attributed to the usage volumes of PAEs in different regions. For example, some developed countries like USA and Europe have introduced strict policy to reduce the level of PAEs in exposure media samples (Das et al., 2014). In addition, the various methods using for estimation should also be considered as a factor for the estimated DI values. The indirect method that estimated the DI values via calculating the concentrations in media would establish the assumption of 100% absorption PAEs in the exposure media in most studies (Clark et al., 2011; Das et al., 2014; Ji et al., 2014), whereas few study has introduced absorption factors for the estimation (Wormuth et al., 2006), leading to large variances of DIs values using different absorption factors. The evaluated DI values of PAEs via dietary intakes and environmental exposure were orders of magnitude lower than the RfD (DEP: 800  $\mu\text{g}/\text{kg}\text{-bw}/\text{day}$ , DNBP: 100  $\mu\text{g}/\text{kg}\text{-bw}/\text{day}$ , BBP: 200  $\mu\text{g}/\text{kg}\text{-bw}/\text{day}$ , DEHP: 20  $\mu\text{g}/\text{kg}\text{-bw}/\text{day}$ ) (US EPA, 1990, 1993a, 1993b, 1993c), not indicating the potential hazard to human health. But note that the exposure estimates are an indicative case as only several typical foodstuffs were collected in this study, and a

comprehensive assessment of human exposure to PAEs through environmental media and food is urgently demanded. Moreover, the RfD values assumed in this study were based on relatively old toxicological studies and new toxicological studies on such compounds might reduce the margin of safety. Additionally, the higher exposure risk of PAEs was observed in toddlers than the other groups via all exposure routes mostly due to the lower body weights, and more attention should be paid for the toddlers.

### 3.6. Limitations and future perspective

Apparently, it is also of note that data for human exposure to PAEs via both environmental matrices and food ingestion in China still remains scarce. In the present study, only several typical foodstuffs were employed to estimate human exposure, and direct exposure from consumer products e.g. consumption of drugs and use of cosmetics, cleaning materials and toys are not taken into account, which may consequently lead to an underestimation of the total daily intake of PAEs. Additionally, the present study focused on a rural area of western China, and the estimates must be varying to a large extent according to different geographical location of the population. Nevertheless, present study was an indicative case, highlighting a scenario of PAEs exposure in a rural area of western China. More high-quality and accurate evaluations such as deducing from urinary metabolite concentrations

**Table 4**  
Estimated daily intake (ng/kg-bw/day) of PAEs via foodstuffs and ambient environments.

	Toddlers				Children				Adults			
	Food	River water	Outdoor air	Indoor air	Food	River water	Outdoor air	Indoor air	Food	River water	Outdoor air	Indoor air
DMP	1.9E-01	4.5E-01	1.7E-03	4.9E-02	6.9E-02	3.0E-01	2.1E-03	4.2E-02	5.4E-02	4.1E-01	4.8E-03	3.6E-02
DEP	1.2E-01	3.5E-01	1.2E-02	1.2E-01	4.7E-02	2.4E-01	1.4E-02	1.0E-01	3.6E-02	3.3E-01	3.4E-02	9.1E-02
BBP	8.9E-03	1.7E-02	1.8E-03	1.6E-02	4.1E-03	1.1E-02	2.1E-03	1.4E-02	3.3E-03	1.6E-02	4.8E-03	1.2E-02
DIBP	2.0E-01	2.3E+00	5.9E-03	3.4E-02	7.8E-02	1.6E+00	6.9E-03	2.9E-02	6.0E-02	2.1E+00	1.6E-02	2.5E-02
DNBP	1.4E+00	5.4E+00	1.1E-02	7.7E-02	5.0E-01	3.6E+00	1.3E-02	6.6E-02	3.9E-01	4.9E+00	2.9E-02	5.7E-02
DEHP	2.8E-01	3.1E+00	2.9E-02	5.7E-01	9.0E-02	2.1E+00	3.5E-02	4.8E-01	7.5E-02	2.8E+00	8.0E-02	4.2E-01
DNOP	5.3E-03	1.3E-02	-	-	1.8E-03	9.0E-03	-	-	1.4E-03	1.2E-02	-	-
PAEs	2.2E+00	1.2E+01	6.2E-02	8.6E-01	7.9E-01	7.8E+00	7.3E-02	7.3E-01	6.2E-01	1.1E+01	1.7E-01	6.4E-01

measurements are desirable for estimating current state of human exposure to PAEs. Furthermore, appropriate risk characterization such as age and gender differences should also be considered.

#### 4. Conclusion

We analyzed the occurrence and bioaccumulation behaviors of PAEs in biological samples as well as ambient environments including river water, indoor and outdoor air in an agricultural area, western China. In addition, human exposure to PAEs was evaluated via food intakes and environmental exposure. PAE levels in biota and environmental samples lay at the low end of the worldwide figures due to the limited anthropogenic activities in this remote area. The biological samples exhibited different PAEs profiles with river water and air samples likely owing to the fast metabolism of some PAEs in organisms. Significant correlations were obtained between the biota and water samples, suggesting that river water heavily impacted the PAEs accumulation in biological samples. There was no obvious trend between  $\log(K_{OW})$  and  $\log(BAFs)$ , and between  $\log K_{OA}$  and  $\log(BAAF_s)$ , which was likely due to fast degradation and metabolism inside living organisms. Water intake was the major contributor for the human intakes of PAEs in toddlers, children and adults. The estimated DIs values were much lower than the reported values and RfD, not indicating the potential hazard to human health.

#### 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.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2019.134264>.

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