RESEARCH ARTICLE

Occurrence and risk assessment of selected phthalates in drinking water from waterworks in China

Xiaowei Liu · Jianghong Shi · Ting Bo · Huiyuan Li · John C. Crittenden

Abstract The first nationwide survey of six phthalates (diethyl phthalate (DEP); dimethyl phthalate (DMP); di-*n*-butyl phthalate (DBP); butyl benzyl phthalate (BBP); bis(2-ethylhexyl) phthalate (DEHP); din-octyl phthalate (DnOP)) in drinking waters from waterworks was conducted across seven geographical zones in China. Of the six target phthalates, DBP and DEHP were the highest abundant phthalates with median (± interquartile range) values of 0.18 ±0.47 and 0.18±0.97 μg/L, respectively, but did not exceed the limit values in China's Standards for Drinking Water Quality. These phthalates in drinking water were generally higher in the northern regions of China than those in the southern and eastern regions. Based on the investigated concentrations, lifetime exposure risk assessment indicated that phthalates in drinking water did not pose carcinogenic and noncarcinogenic risks to Chinese residents, even under the conservative scenario (with 95th percentile risk). In addition, we found that DEHP contributed the greatest risk to the total exposure risk of all the selected phthalates and oral ingestion was the main exposure route for phthalates in drinking water.

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Introduction

In recent years, reproductive and developmental toxicities of phthalates have been a cause of concern (Howdeshell et al. 2008; Lovekamp-Swan and Davis 2003), and these chemicals have been suspected of endocrine-disrupting effects on humans (Latini 2005; Lyche et al. 2009; Matsumoto et al. 2008). In addition, bis(2-ethylhexyl) phthalate (DEHP) has also been identified as a potential carcinogenic compound (IARC 2012). To reduce adverse risk of human exposure to phthalates, some regulations limiting their use and maximum concentration levels in children articles and food packages have been proposed (EC 2005; NSPC 2008). However, phthalates are produced in high volume (US EPA 2012), and they primarily, as plasticizers, are added to poly(vinyl chloride) (PVC) products for increasing the flexibility and durability of consumer products and industrial products (Latini 2005). Worldwide annual consumption of phthalates was approximately five million tons in 2010 (Guo et al. 2012). In China, over 1.7 million tons of phthalates were annually consumed in 2009 (Qian 2010), accounting for almost one third of the global consumption. Those phthalates can be readily released to the environment during production, usage, and final disposal of plastic consumer products and industrial products because they are nonchemically bonded to polymers. In addition, the biosolid application and wastewater treatment plant effluent are also the main contributors of phthalates in environment (Gao et al. 2014; Sablayrolles et al. 2013). Phthalates are refractory to biodegradation (Abdel daiem et al. 2012), which increases their persistence in environment. Their continuous release and persistence to the environment have resulted in potential exposure to human via indoor air, surface

water, groundwater, food, personal care products, etc. (Guo et al. 2012, 2014; Sablayrolles et al. 2013; Xie et al. 2007; Zeng et al. 2008). Phthalates also have been detected in drinking water (Benotti et al. 2008; Loraine and Pettigrove 2006; Santana et al. 2014). Phthalates in source water are the main contributors in drinking water (Liu et al. 2014). In addition, some plastic pipes and slats are used in waterworks, which potentially increase phthalate release into drinking water during the treatment processes. Some studies have reported that traditional waterworks did not efficiently remove phthalates and even contaminated those treated water (Li et al. 2010a; Yu et al. 2005). For reducing the risk of phthalates contamination in drinking water, some countries and organizations have regulated the guideline values of phthalates in drinking water (in China, 8, 3, and 300 μg/L for DEHP, DBP, and DEP, respectively (NSC 2006); in WHO, 8 μg/L for DEHP (WHO 2011); in the USA, the maximum contaminant level (MCL) value (6 μg/L) for DEHP (US EPA 2006); in Japan, 100, 200, and 500 μg/L for DEHP, DBP, and BBP, respectively (Wakayama 2004)). In eastern and northern China, phthalates have been detected in 13 drinking water samples and 10 drinking water samples, respectively, ranging from no detection to 28.9 μg/L (Hu et al. 2013; Li et al. 2010a, b; Shi et al. 2012). No potential health risks to humans were identified by determining the androgen and thyroid receptor agonistic and antagonistic potencies based on reporter gene assay in eastern China (Hu et al. 2013; Shi et al. 2012).

In order to make a throughout risk examination of phthalates that might pose to Chinese residents via drinking water exposure, we conducted the first nationwide survey and risk assessment of phthalates in drinking water from waterworks across seven geographical zones in China. Six phthalates (diethyl phthalate (DEP); dimethyl phthalate (DMP); di-*n*-butyl phthalate (DBP); butyl benzyl phthalate (BBP); bis(2-ethylhexyl) phthalate (DEHP); din-octyl phthalate (DnOP)) were investigated in this study. The objectives of this study were as follows: (1) to examine the occurrence of phthalates in drinking water in different regions of China and (2) to identify the potential risk posed on Chinese residents via drinking water exposure. This study provides the scientific information for regulators, environmental scientists, and even for the public about whether phthalates in drinking water threaten the health of Chinese residents.

Materials and methods

Sampling location and sampling methods

The survey of six phthalates was conducted over the period of December 2009–May 2012 across seven geographical zones in China: Northeast China (NEC), North China (NC), Northwest China (NWC), Southwest China (SWC), South China (SC), East China (EC), and Central China (CC) (Fig. S1).

Two hundred and twenty-five drinking water samples were collected during two sampling campaigns (Table S1). A total of 117 water samples were collected from December 2009 to March 2011, and the others were collected from August 2011 to May 2012. In the second sampling campaign, 100 water samples were collected from the waterworks as in the first sampling campaign; other water samples were collected in different waterworks, because outdated waterworks had been updated or closed in certain cities. These sampling sites were averagely located in the provincial capitals in mainland China and some cities, such as Qingdao, Xiamen, etc., having similar sizes with these provincial capitals (Fig. S2). All waterworks use the treatment processes of flocculation, sedimentation, filtration, and chlorine disinfection. The seasonal influence of the concentration of phthalates in drinking water was not considered during the sampling campaigns. The drinking water samples were collected in Teflon-capped amber glass bottles from each sampling site and transported immediately to the laboratory in coolers at 4 °C for further pretreatment and analysis.

Chemicals and reagents

Two kinds of EPA Phthalate Mix (200 mg/L each component in methanol and 2000 mg/L each component in *n*-hexane) containing DMP, DEP, DBP, BBP, DnOP, and DEHP and the internal standard deuterated bis(2-ethylhexyl) phthalate (DEHP-d_4) were purchased from Sigma-Aldrich (Bellefonte, PA, USA). Stock solutions of the six phthalates were prepared in HPLC-grade methanol (4 mg/L) and HPLC-grade *n*-hexane (40 mg/L) and stored at −20 °C. Working standard solutions (10–2000 μg/L) in *n*-hexane for direct injection calibration were prepared by serial dilution of the stock solutions and stored at 4 °C. Standard solutions in methanol were also prepared for the recovery experiment and stored at 4 °C. The organic solvents used in this experiment, including methanol, diethyl ether, and *n*-hexane, were HPLC grade and obtained from Mallinckrodt Baker, USA.

Sample pretreatment and instrumental analysis

The pretreatment procedures for water samples were described in detail in our previous study (Liu et al. 2014). Here, we briefly presented these procedures. Before extraction, 1-L water samples were filtrated through glass fiber filters (GF/F, 0.7-μm pore size, Whatman). Oasis hydrophilic lipophilic balance (HLB) cartridges (3 mL, 200 mg, Waters) were used to extract the six compounds from the water samples. Finally, the extracts were reconstituted with l mL of *n*-hexane.

The target phthalates were analyzed using a Varian 3800 gas chromatograph coupled with a triple quadrupole analyzer mass spectrometer (GC-MS). A flexible fused silica capillary column (30 mm×0.32 mm×0.11 μm, Varian) was used for the

separation of target compounds. The detailed procedure and specific parameters for the instrumental analysis were described in our previous work (Liu et al. 2014).

Quantification of the target compounds was conducted using the internal standard calibration methodology. The calibration was performed with the eight standard mixtures ranging 10–2000 μg/L. The calibration solution and the final extract were spiked with the internal standard DEHP-d$_4$ (Casajuana and Lacorte 2003) at a concentration level of 0.1 μg/mL for quantification prior to GC-MS.

Quality assurance and quality control

Phthalates readily migrate from plastic products to environmental media and are potentially present in the laboratory air (Xie et al. 2006). In order to reduce the potential risks of the analytes contaminated during the process of the entire analysis, the plastic materials were not used in our experiments and the pretreatments of all samples were carried out in a super-clean workbench (HDL, Beijing). Procedure blank experiment in each batch experiment was performed to determine whether contaminations were caused by the experimental materials (e.g., *n*-hexane, methanol/diethyl ether, Milli-Q water, and HLB cartridges) and the laboratory air. The procedure blank analysis was described in our previous report in detail (Liu et al. 2014) and in Supplementary information (SI, Tables S2–S4), which indicated that the contribution of phthalates in methanol/ diethyl ether, HLB cartridge, Milli-Q water, and the air in workbench to the real samples was less than 5 %, while *n*-hexane contributed approximately 20 % of DMP, DEP, BBP, and DnOP to the analytes. Thus, the contribution from *n*-hexane was excluded from the result of the instrument analysis. Due to the big sample sets analyzed, one in three of samples was analyzed in duplicate and relatively satisfactory repeatability was achieved (relative errors less than 50 %) (Fig. S3). Matrix spike recoveries were checked by spiking 1-L field water samples with the standard solutions with each target compounds at three concentrations (0.05, 0.1, and 0.5 μg/L). The recoveries of the six phthalates in the spiked samples ranged 54.9–94.6 % (*n*=6) with relative standard deviation (RSD) values less than 15 % (Table S5). Standards and solvent blank were analyzed after every ten samples to ensure the stability and accuracy of instrumental analysis. Method detection limits (MDLs) ranging from 0.002 to 0.01 μg/L (Table S5) were determined using the signal to noise ratio (SNR) larger than 3. Concentrations below MDLs were assigned to half of the MDL values for statistical analysis.

Calculations of human exposure to phthalates and risk assessment

Humans are generally exposed to phthalates via oral ingestion of drinking water, dermal contact with water, and inhalation of water vapor during bathing or showering. The intake dose of phthalates via ingestion of drinking water can be calculated as follows:

$$\mathrm{ADI_{oral}} = \frac{C_\mathrm{w} \times \mathrm{IR_w} \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{BW} \times \mathrm{AT}}$$

where $\mathrm{ADI_{oral}}$ is the average daily intake dose of phthalates via oral ingestion of drinking water (μg/kg/ day), C_w is the concentration of phthalate in drinking water (μg/L), $\mathrm{IR_w}$ is the ingestion rate of drinking water (in this study, drinking water only includes tap water) (L/day), EF is the exposure frequency (days/year) (for residents, usually daily—365 days/year), ED is the exposure duration for lifetime (years), and AT is the average time of exposure (days) (AT for noncarcinogenic effects is ED year×365 days/year; AT for carcinogenic effects is lifetime year×365 days/year).

The estimated daily absorbed dose of phthalates via dermal contact during bathing or showering is as follows:

$$\mathrm{ADI_{derm}} = \frac{C_\mathrm{w} \times \mathrm{SA} \times K_\mathrm{P} \times \mathrm{ET} \times \mathrm{EF} \times \mathrm{ED} \times \mathrm{CF}}{\mathrm{BW} \times \mathrm{AT}}$$

where $\mathrm{ADI_{derm}}$ is the average daily intake dose by dermal contact with chemical in water (μg/kg/day), SA is the skin surface area available for contact (cm^2), K_p is the dermal permeability coefficient (cm/h), ET is the exposure time during bathing or showering (h/day), CF is a volumetric conversion factor (1 L/1000 cm^3), and BW is the body weight (kg).

The estimated daily intake dose of phthalates via inhalation of water vapor during bathing or showering is the following equation:

$$\mathrm{ADI_{inhal}} = \frac{C_\mathrm{air} \times \mathrm{IR_{air}} \times \mathrm{ET} \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{BW} \times \mathrm{AT}}$$

where $\mathrm{ADI_{inhal}}$ is the average daily intake dose of phthalates via inhalation of water vapor during bathing or showering (μg/kg/day), C_air is the concentration of phthalates in vapor phase in bathroom (μg/L), and $\mathrm{IR_{air}}$ is the inhalation rate during bathing or showering (L/h). The concentration of phthalate in vapor phase (C_air) was estimated based on the method reported by Moya et al. (1999) and Wang et al. (2007a), which was described in detail in the SI and Table S6. Considering the differences in body height, weight, and lifestyle in different regions of China, exposure factors for population from specific region were used from the Chinese population exposure handbook (MEPC 2013) (Table S7). The chemical-specific parameters used in exposure assessment are listed in Table S8.

As for the risk classification of these phthalates, the International Agency on Research on Cancer has reclassified DEHP as an agent being possibly carcinogenic to humans (group 2B) (IARC 2012), and there is no weight of evidence for

carcinogenicity of other phthalates. Thus, the noncarcinogenic risk assessment for DEP, DBP, DEHP, DnOP, and BBP and the carcinogenic risk assessment for DEHP were conducted.

The noncarcinogenic risk of phthalates can be characterized based on the hazard index (HI) approach from the US EPA (1989), comparing exposure doses with toxicity-based benchmark values. The reference doses (RfDs) for the phthalates were used as the benchmark values of toxicity (Table S8). Hazard quotient (HQ) value for specific chemical was calculated as follows:

$$HQ = \frac{ADI}{RfD}$$

For the integrated risk of chemical mixtures, the exposure risk of all target chemicals (HI) is the sum of HQ of each chemical.

$$HI = \sum HQ_i$$

where HQ_i is the risk for the ith chemical. The reference doses include reference dose for oral ingestion (RfD_o), reference dose for dermal contact ($RfD_d = RfD_o \times ABS_{gi}$, ABS_{gi} is the fraction of chemical absorbed in the gastrointestinal tract (unitless)) (US EPA 2004) and reference dose for inhalation (RfC_i, mg/m^3). Due to the reference dose for these phthalates via inhalation exposure being unavailable, the risks caused by inhalation exposure were not included in the total noncarcinogenic risk values. The total noncarcinogenic risk of all exposure routes is the sum of HI of each exposure route (US EPA 1989). When the exposure level exceeds the risk threshold (i.e., the HI exceeds unity), the potential risk of the target chemicals is of concern.

Due to the low-dose exposure of DEHP in drinking water, the carcinogenic risk assessment of DEHP was conducted according to the linear low-dose carcinogenic risk equation:

$$Risk = ADI \times SF$$

where Risk is a unitless probability of an individual developing cancer (unitless) and SF is the slope factor (μg/kg/day)$^{-1}$. The slope factors include slope factor for oral ingestion (SF_o (μg/kg/day)$^{-1}$), slope factor for dermal contact (SF_d (μg/kg/day)$^{-1}$), and slope factor for inhalation (SF_i (μg/kg/day)$^{-1}$). The SF_d and SF_i were estimated as follows (US EPA 1989; US EPA 2004), respectively:

$$SF_d = \frac{SF_o}{ABS_{gi}}$$
$$SF_i = \frac{IUR \times BW}{DAIR}$$

where IUR is the inhalation unit risk (μg/m^3)$^{-1}$ and DAIR is the inhalation rate for adult (m^3/day). The estimated cancer

risk levels below 1×10^{-6} are considered to be negligible, risk values between 1×10^{-4} and 1×10^{-6} are acceptable levels, and risks above 1×10^{-4} should be considerably concerned (US EPA 1991). The specific parameters for risk assessments are listed in Tables 7S and 8S.

Due to likely variations of contamination levels of these chemicals in different waterworks, Monte Carlo simulation (5000 runs) was used to determine the variability of the risk distribution for human exposure to phthalates.

Statistical analysis

One-sample Kolmogorov-Smirnov (K-S) test was used to assess the normal distribution of data. The results showed that the concentrations of the six phthalates were not normally distributed in most cases, so the nonparametric Kruskal-Wallis H test and the rank transform method combined with one-way ANOVA were used to assess significant differences among various independent samples. Statistical tests were performed using the SPSS 13.0 for Windows (SPSS Inc.), and the statistical significance level was set to be 0.05.

Results and discussion

Occurrence of phthalates in drinking water

Of the six target phthalates, the detection frequencies of DEP, DBP, DEHP, and DMP (Table 1) were all above 88 %, indicating that phthalates were ubiquitous in drinking water in China. DBP and DEHP had the highest contamination levels with median ($\pm$ interquartile range, IQR) concentration of 0.18 ± 0.47 and 0.18 ± 0.97 μg/L, respectively. In spite of the high detection frequencies, over 60 % of these phthalates were mainly present at relatively low concentrations (Fig. S4). The concentrations of DEP, DBP, and DEHP did not exceed the limit values in China's Standards for Drinking Water Quality (8 μg/L for DEHP, 3 μg/L for DBP, and 300 μg/L for DEP) and the guideline value of 8 μg/L for DEHP regulated in WHO (WHO 2011); only DEHP at one site in NEC had a concentration of 5.51 μg/L, which is close to the maximum contaminant level (MCL) value (6 μg/L) in the National Primary Drinking Water Regulation of the USA. BBP and DnOP had the lowest detection frequencies of 45.4 and 50.7 %, respectively, and the lowest concentration levels with median ($\pm$ IQR) concentrations of 0.001 ($\pm$0.033) and 0.001 μg/L ($\pm$0.018), respectively.

Compared to phthalates in drinking water in other countries (Table 1), their mean concentrations in drinking water in China were slightly higher than those in the USA, with exception of DEP and BBP which have relatively low concentrations in China. Phthalates in drinking water in China were slightly higher than those in Spain except DBP with similar

Table 1   Summary of the six phthalates in drinking water and comparisons with those in other countries

Compound	N	Freq (%)	Max (µg/L)	Median±IQR (µg/L)	Mean (µg/L)	Literature values (mean, µg/L)		
						USA	Spain	Portuguese
DEP	225	88.4	0.19	0.021±0.037	0.035	<MRL[b]; 0.16[c];	0.38[d]; 0.20[e]	– [f]; 0.19[g]
DBP	225	99.6	1.56	0.18±0.47	0.35	0.18[c]	0.63±0.26[d]; <0.42[e]	n.d.[f]; 0.52[g]
DEHP	225	94.2	5.51	0.18±0.91	0.77	0.34 (n.d.–2.64)[c]	<LOD[d]; <0.45[e]	n.d.–0.19[f]; 0.06[g]
DnOP	225	50.7	0.24	0.001±0.018	0.026	–	–	–
DMP	225	93.9	0.76	0.035±0.086	0.071	0.04[c]	0.02±0.013[d]; n.d.[e]	– [f]; 0.04[g]
BBP[a]	108	45.4	0.35	0.001±0.033	0.026	<MRL[a,b]; 0.18 (n.d.–0.91)[c]	<LOD[d]; n.d.[e]	– [f]; 0.03[g]

The method reporting limit (MRL) is 0.12 and 0.05 µg/L for DEP and BBP, respectively; the LOD is 0.46 and 0.19 for DEHP and BBP, respectively.

N number of samples, *Freq* frequency of detection, *Max* maximum concentration detected, *Median* median concentration, *IQR* interquartile range, *n.d.* not detected

[a] BBP was not selected as a target compound in the first sampling campaign (from December 2009 to April 2011)

[b] Southern California (Loraine and Pettigrove 2006)

[c] Nineteen waterworks across the USA (Benotti et al. 2008)

[d] Central Spain (Domínguez-Morueco et al. 2014)

[e] Northwest Spain (Regueiro et al. 2008)

[f] Lisbon and its neighboring cities (Santana et al. 2014)

[g] Serôdio and Nogueira (2006)

concentrations to Spain. DEHP and DMP in China were slightly higher than those in Portugal, DEP in drinking water had

relatively low concentrations in China, and DBP and BBP in China were comparable to Portugal. To sum up, the

Fig. 1 Distribution of the six phthalates in drinking water from waterworks in the seven geographical zones of China (*NEC* Northeast China, *NC* North China, *EC* East China, *SC* South China, *NWC* Northwest China, *SWC* Southwest China, *CC* Central China). *Box plots* show the 25th and 75th percentiles (*bottom* and *top of the box*), median (*solid line within the box*), and mean (*dashed line within the box*). The *bottom* and *top whisker caps of the boxes* represent the 10th and 90th percentiles. Outliers (*black circle*) are values that lie outside the 10th and 90th percentiles. The number and detection frequencies of samples are given *above* and *below the boxes*, respectively
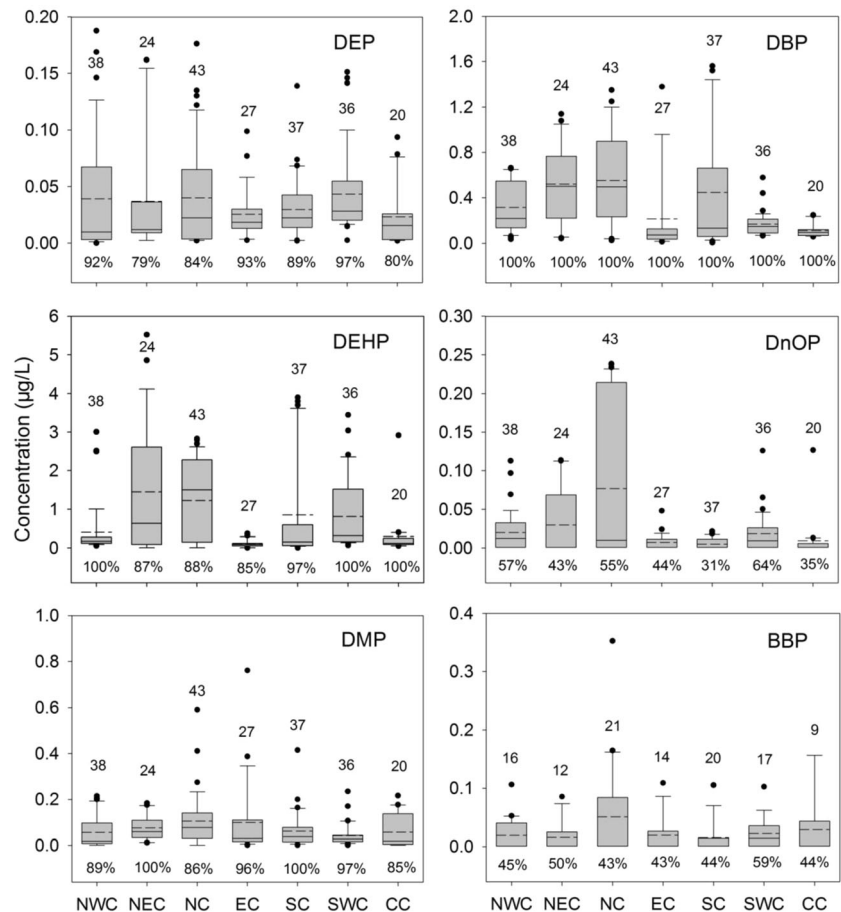
Table 2 Hazard index (HI) of human exposed to the six phthalates in drinking water

Region		DEP	DBP	DEHP	DnOP	BBP	Total phthalates
NWC	Mean	2.09E−06	5.59E−05	3.68E−04	8.66E−05	2.10E−06	5.14E−04
	50th	2.69E−07	3.93E−05	1.64E−04	8.68E−05	1.12E−06	3.49E−04
	95th	8.02E−06	1.71E−04	1.36E−03	3.22E−04	7.86E−06	1.55E−03
NEC	Mean	1.08E−06	1.56E−04	1.55E−03	5.27E−04	2.29E−06	2.23E−03
	50th	3.84E−07	7.22E−05	1.27E−03	4.67E−05	3.51E−07	1.70E−03
	95th	4.14E−06	5.66E−04	3.94E−03	1.49E−03	8.76E−06	4.73E−03
NC	Mean	1.68E−06	1.69E−04	1.18E−03	1.27E−03	4.70E−06	2.63E−03
	50th	5.07E−07	8.35E−05	1.19E−03	7.29E−05	4.51E−06	1.70E−03
	95th	7.21E−06	5.94E−04	3.51E−03	3.54E−03	2.29E−05	5.78E−03
EC	Mean	5.64E−07	1.69E−04	3.51E−04	6.47E−05	4.03E−06	5.89E−04
	50th	4.95E−07	2.70E−05	6.91E−06	6.43E−05	6.76E−07	2.80E−04
	95th	1.34E−06	6.29E−04	1.31E−02	2.27E−04	1.44E−05	1.91E−03
SC	Mean	1.19E−06	1.52E−04	9.75E−04	6.39E−05	2.65E−06	1.19E−03
	50th	5.54E−07	4.17E−05	2.25E−04	8.58E−05	5.50E−07	4.53E−04
	95th	4.29E−06	5.63E−04	3.67E−03	2.54E−04	1.02E−05	4.06E−03
SWC	Mean	9.10E−07	3.39E−05	7.74E−04	9.08E−05	2.00E−06	9.02E−04
	50th	6.73E−07	2.41E−05	1.94E−04	9.11E−05	1.12E−06	3.69E−04
	95th	2.40E−06	8.67E−05	3.04E−03	3.31E−04	7.00E−06	3.13E−03
CC	Mean	6.23E−07	2.13E−05	2.71E−04	3.76E−05	5.27E−06	3.36E−04
	50th	2.88E−07	1.70E−05	1.24E−04	1.50E−05	5.43E−07	1.89E−04
	95th	2.21E−06	4.46E−05	8.66E−04	1.34E−04	2.02E−05	9.55E−04
The whole country	Mean	1.08E−06	1.06E−04	1.08E−03	2.49E−04	3.02E−06	1.44E−03
	50th	4.36E−07	3.98E−05	2.26E−04	4.71E−05	5.39E−07	4.56E−04
	95th	4.01E−06	4.03E−04	3.66E−03	9.59E−04	1.19E−05	4.58E−03

95th percentile is reasonable maximum exposure (RME), which is used to demonstrate a conservation exposure case scenario

contamination levels of DEHP and DMP in drinking water in China were relatively higher compared to the USA, Spain, and Portugal; other phthalates such as DEP, DBP, and BBP in drinking water China were slightly lower than or similar to those in other countries.

Phthalates in drinking water in different regions

The contamination levels of phthalates in drinking water varied among different regions in China (Fig. 1). DEP in drinking water from SWC was the highest among these investigated regions ($p < 0.036$) (Table S9). DBP in drinking water from the northern part of China including NEC, NC, and NWC was clearly higher than those from the southern part (SC and SWC) and the central part (EC and CC) ($p < 0.042$) (Table S10). DEHP in drinking water from NEC and NC was higher than those from NWC, EC, and CC ($p < 0.029$) (Table S11). DnOP in drinking water from NC was higher than those from other regions ($p = 0$); DMP and BBP from NC were higher than those from other regions, but not significant ($p = 0.129$ for DMP and $p = 0.961$ for BBP) (Tables S12–S14). The six phthalates in drinking waters from NWC and

SWC were detected with higher frequencies compared to other regions. The highest median (± IQR) concentrations of DBP (0.50±0.54 μg/L) and DEHP (1.50±2.10 μg/L) were observed in NC; the second highest median (± IQR) concentrations of DBP (0.50±0.51 μg/L) and DEHP (0.63± 2.44 μg/L) were found in NEC, which was comparable to another report of frequently high contamination levels of DEHP and DBP in surface waters in NEC (Chen et al. 2012). To sum up, the contamination levels of the six phthalates in the northern regions of China (NC, NWC, and NEC) were generally higher than those in the southern and eastern regions (EC, SC, SWC, and CC), in spite of similar detection frequencies.

Water quality of drinking water is directly related to the quality of source water for waterworks. In our previous report (Liu et al. 2014), higher concentrations of phthalates in source water were found in the northern regions of China (NC, NWC, and NEC), as compared to the southern regions of China (EC, SC, SWC, and CC). By consideration of the economic development, the integrated waste disposal rate, and the availability of water resource between the northern and southern regions of China, the shortage of surface water resource was likely to

Fig. 2 Probabilistic carcinogenic risk of DEHP in drinking water exposed to Chinese adult
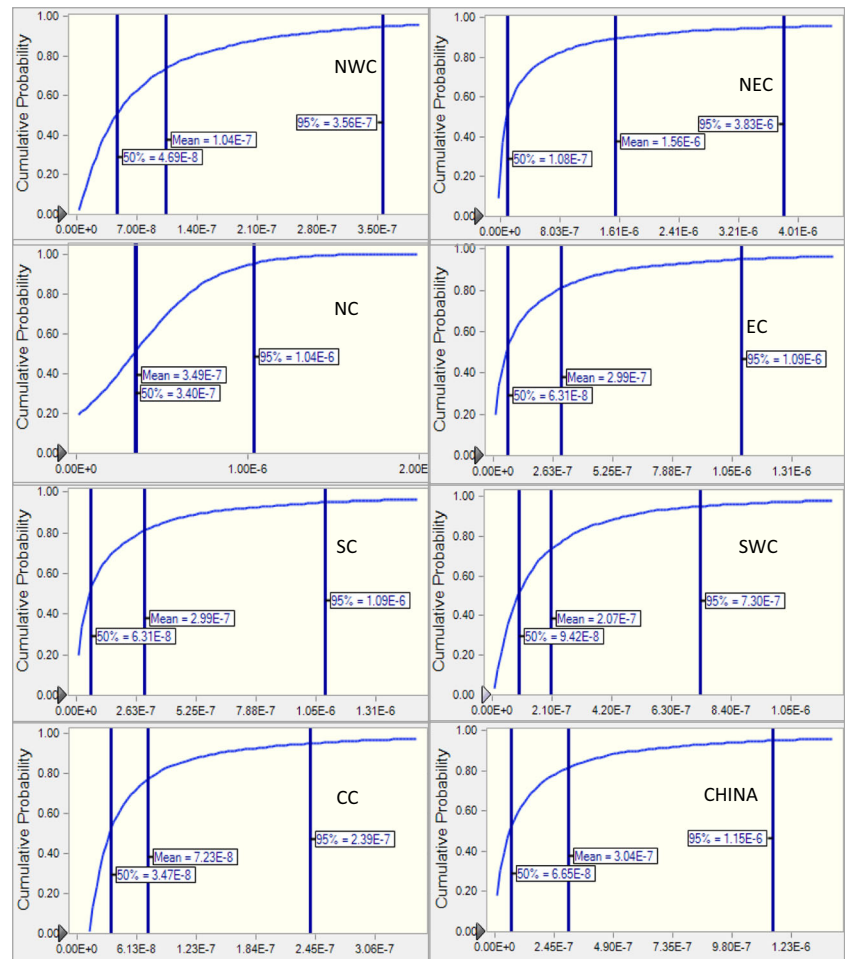
be the main reason causing the high occurrence of these phthalates in the northern regions of China (NC, NWC, and NEC). In addition, the high presence of phthalates in groundwater source in NC (Liu et al. 2014) also might make a big contribution to the phthalates in drinking water.
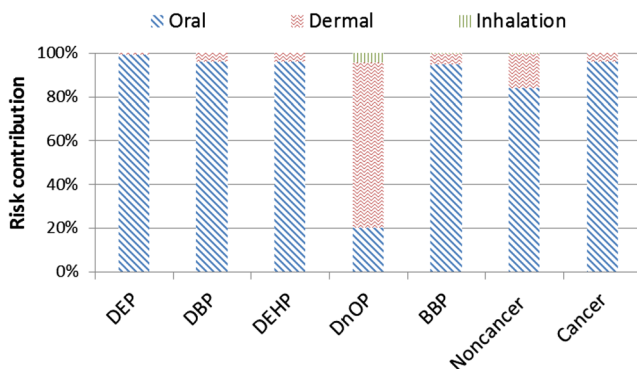

Fig. 3 Risk contribution of each exposure route for human exposed to the selected phthalates. Noncancer: the total noncarcinogenic risk of the five selected phthalates; cancer: carcinogenic risk caused by DEHP in drinking water

Human health risk of phthalates to Chinese residents

The risk assessment for the selected phthalates via drinking water exposure was estimated across the seven geographical regions in China using the measured concentrations incorporating the published historical data since 2006 (Hu et al. 2013; Li et al. 2010a, b, 2013; Liu et al. 2013; Lu et al. 2007; Shao et al. 2008; Shi et al. 2012; Wang et al. 2007b; Wang 2007; Zhang et al. 2008). The risk levels of central tendency and reasonable maximum exposure risk levels were used to determine the probabilistic risks of these phthalates. Here, we mean that central tendency risks are based on the mean and median phthalate concentrations. Based on the central tendency exposure estimation with the mean and median values (Table 2), the HI of the selected phthalates in these regions and in the whole country did not exceed the risk threshold "1"; even in the conservative scenario (reasonable maximum exposure with 95th percentile risk), the noncarcinogenic risk levels of total phthalates were still one or two orders of magnitude lower than the risk thresholds (Table 2). The carcinogenic risk caused by DEHP in drinking water in NWC, NC, EC, SWC, and CC was negligible with 95th values of the risk lower than

1×10^{-6}; the carcinogenic risk was acceptable in NEC, SC, and the whole country with 95th values of the risk lower than 1×10^{-4} (Fig. 2). Therefore, these phthalates in drinking water did not pose adverse human health risks of concern in China. In addition, the risk identification by androgen and thyroid receptor agonists and antagonists through drinking water in eastern China also has indicated that phthalates imposed low risk to human health (Hu et al. 2013; Shi et al. 2012). Of these target chemicals, DEHP contributed the greatest risk to the total exposure risk (Table 2), which was comparable to the highest contribution from DEHP via dietary intake in China (Guo et al. 2012). By comparing risk levels among different regions, it was found that the risk of phthalates in drinking water in NEC was the highest (Table 2 and Fig. 2).

In addition, there were three main routes for exposure of phthalates in drinking water to human bodies. Due to the reference concentrations for phthalates via inhalation exposure being unavailable, the noncarcinogenic risk estimation via inhalation exposure during bathing or showering was not conducted. However, the carcinogenic risk via inhalation exposure was included. The highest risk contribution was via oral ingestion exposure, which accounted for more than 90 %, except for DnOP (Fig. 3). For DnOP, due to its high permeability, dermal contact during bathing or showering was the main exposure route, accounting for around 75 % of the total risk. However, the dermal permeability coefficient for DnOP was estimated by an empirical predictive correlation (US EPA 2004), which might not be accurate. A measured value would be more appropriate for determining the main contribution route of DnOP to human health risks via drinking water exposure. Inhalation ingestion during bathing or showering contributed the lowest risk of developing cancer with only 0.03 % of risk contribution (Fig. 3). In contrast, inhalation ingestion of DEHP in indoor dust was identified as the main exposure route in southern China (Kang et al. 2012).

Although phthalates were frequently detected in drinking water in China, these chemicals via drinking water exposure did not pose a significant risk on human health, even for the highest possible exposure case (95th percentile risk). In addition, Chinese people are used to typically boil water before drinking it, so these semi-volatile chemicals will be partly evaporated during water boiling. More than 80 % removal efficiencies of phthalates have been reported by boiling water (Hu et al. 2013; Shi et al. 2012). Therefore, the risk of these phthalates in drinking water might pose lower risks on Chinese people via drinking boiled water compared to directly drinking tap water. Children and other sensitive human groups are likely to be at higher exposure risk than adults. However, currently, due to less population information and drinking water exposure data available for Chinese children group, the impact was not included in our study.

Conclusions

The nationwide survey of phthalates in drinking water indicated that DBP and DEHP were the highest abundant phthalates in drinking water in China but did not exceed the limit values in China's Standards for Drinking Water Quality. The contamination levels of the target phthalates in the northern regions of China (NC, NWC, and NEC) were generally higher than those in the southern and eastern regions (EC, SC, SWC, and CC). The human health risk assessment demonstrated that these phthalates did not pose risks of concern to Chinese residents via drinking water exposure, even for the highest possible exposure. The oral ingestion was the main exposure route, and DEHP made the biggest contribution to the total exposure risk.

Conflict of interest There are no conflicts of interest.

Compliance with ethical standards We confirm that this manuscript complies with the ethical rules applicable for *Environmental Science and Pollution Research*. It is the original work of the authors, and all authors mutually agree that it should be submitted to this journal. It has not been submitted to this journal before and has not been submitted to other journals.

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