The occurrence of home and personal care products in the Haihe River Catchment and estimation of human exposure

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Abstract A sub-catchment of the Haihe River basin goes through the Beijing-Tianjin region with a population of 26 million, therefore, the use and release of home and personal care product ingredients (HPCPs) to the river catchment could be potentially substantial. Many HPCPs have been shown to be toxic to human and animals. So, it is essential to know the exposure level of HPCPs in the river basin. The average concentrations of five preservatives, three disinfectants and an antioxidant were found to be 398, 352 and 77.7 ng L^{-1}, respectively, in the dry season. The chemical concentrations in the effluents of wastewater treatment plants (WWTPs) and untreated wastewater discharge were respectively ca. 1.3-2.2 and 1.6-7.5 times higher than those in river water. The mass flux of ∑HPCPs has been estimated to be 8.7 g/hr at the outfall of the Shahe Reservoir and 181 g/hr and 214 g/hr at the estuary of the Haihe River and Yongdingxin River to Bohai Bay, respectively. The attenuation of ∑HPCPs was over 79% along the Wenyu River. By using the backward method, the estimated average loadings to WWTPs ranged from 0.51 to 2.0 mg/day/cap for the various individual compounds. They were 1-3 orders of magnitude higher than the estimation from the forward calculation for parabens. This indicates the possible underestimation of chemical usage and human exposure levels by the current published studies or the probably additional industrial release to the target catchment. Such a study provides useful information for the development of chemical management approaches and indicates that further research is needed to improve the estimation of HPCPs usage and emissions to aquatic environment.

Keywords: Haihe River basin; parabens; HPCPs; mass flux; human exposure

1. Introduction

Global concern has been raised over organic micropollutants due to their environmental contamination and risks (Schwarzenbach et al., 2006). During the past decades, China has focused on pollution investigation and control of conventional priority pollutants, such as polychlorinated biphenyls (Chen et al., 2014; Zhang et al., 2004), polycyclic aromatic hydrocarbons (Tao et al., 2007; Sun et al., 2017; Zhu et al., 2015), pesticides (Ouyang et al., 2016a; 2017) and herbicide (Ouyang et al., 2016b; 2016c). However, researches on some emerging contaminants, such as home and personal care products (HPCPs), are still relatively limited.

HPCPs are a class of contaminants of emerging concern which include a diverse collection of compounds, such as disinfectants, preservatives, antioxidants and fragrances. (Brausch and Rand, 2011; Bu et al., 2013). These chemicals are widely included in cosmetics, foodstuffs and pharmaceuticals (e.g. parabens) etc. (Guo and Kannan, 2013; Liao et al., 2013a; Ma et al., 2016; Zhu et al., 2016). Human exposure to these chemicals occurs on a daily basis. The detection of HPCPs is ubiquitous across aquatic environments worldwide (Liu and Wong, 2013). Wastewater treatment plants (WWTPs) are important point sources of HPCPs in aquatic systems, as they can only partially remove HPCPs that are released with domestic and industrial wastewater (Boxall et al., 2003; Chen et al., 2017). Diffusive release may additionally exist through untreated wastewater (UW) (Wang et al., 2015).

Continuous exposure to HPCPs has been linked with detrimental effects on aquatic ecosystems and human health (Brausch and Rand, 2011; Guo et al., 2014;). Studies have suggested that parabens (the esters of p-hydroxybenzoic acid) may act as endocrine disruptors in aquatic systems (Yamamoto et al., 2011). And the occurrence of parabens in human serum, placenta, urine and breast tumors has been reported by the previous studies (Darbre et al., 2004; Sandanger et al., 2011; Wang et al., 2013). Disinfectants, such as triclosan (TCS) and triclocarban (TCC), have been shown to inhibit the growth of algae (Yang et al., 2008). TCS is linked to the change in sex ratios and fin length of medaka (Brausch and Rand, 2011; Foran et al., 2000). US FDA (Food and Drug Administration) has banned the use of TCS and TCC in soaps due to their potential health risks (FDA, 2016). Butylated hydroxyanisole (BHA), an antioxidant, has been suggested to be carcinogenic to rodents and humans as well as an environmental endocrine disruptor (IARC, 1987; Jimenez, 1997; Williams et al., 1999).

Therefore, it is essential to investigate the environmental concentration and potential human exposure level of HPCPs. A backward-calculation method for estimating chemical release to rivers based on the measurement of chemicals in surface water was firstly applied on the illicit drug (Zuccato et al., 2005). It was then extended on alcohol, nicotine, caffeine, plasticizers and pharmaceuticals (Gonzalez-Marino et al., 2017; Rodriguez-Alvarez et al., 2015; Senta et al., 2015; Verlicchi et al., 2014) for a rough estimation of the usage. The methodology was also called wastewater-based epidemiology. Another more commonly used method for estimating the chemical

usage and emission is based on market data of products or materials being sold or consumed. This method is more straightforward and has been applied on different types of chemicals including HPCPs, which can be called as forward calculation (Zhu et al., 2016; Shen et al., 2013; Zhang et al., 2015). The backward calculation can be applied to validate the forward calculation. However, such validation has never been conducted by previous studies, to the best of the authors' knowledge.

Approximately 156 million people live in the Haihe River basin in China (Rong et al., 2016), in which the Beijing-Tianjin-Hebei region is one of the regions with the densest population and the largest economy in China and represents an important industrial base in Northern China. The consumption and release of HPCPs could potentially be substantial in this region, but relevant studies are limited (Zhu et al., 2016). Monitoring data for TCS and TCC across China are relatively abundant compared to other HPCPs (Zhao et al., 2013). On the contrary, measurements of parabens in freshwaters across China are limited with few data on BHA. Most existing monitoring campaigns on HPCPs have focused on catchments in the Pearl River Delta (PRD) (Gong et al., 2011; Peng et al., 2008; Zhao et al., 2013). Relevant studies on the Haihe River basin are limited, although the emission of HPCPs is potentially high whilst river discharge flow rates could be lower compared to rivers in the PRD. The usage of TCS, TCC across China and levels of daily human exposure to some parabens through different routes have been investigated by surveys of the content of parabens in products (Guo and Kannan, 2013; Liao et al., 2013a; Ma et al., 2016; Zhu et al., 2016). However, these estimates have not been validated regionally.

105 This study aims to investigate the occurrence, spatial distribution and mass flux of
106 nine typical HPCPs in a sub-catchment in the Haihe River basin in the dry season, as
107 well as the potential human exposure level of HPCPs. The backward-calculation
108 method has been introduced to trace back the loading of HPCPs into WWTPs by
109 using the concentrations of compounds determined in this study. The results were then
110 compared with those from the forward calculation. Such method can potentially be
111 used to validate the estimation of usage and emissions of chemicals that mainly derive
112 from anthropogenic sources and are released with domestic wastewater. This
113 information would be useful to support the regional management of water
114 contaminants.

115 **2. Materials and methods**

116 *2.1 Study area and sample collection*

117 The Haihe River basin covers Beijing, Tianjin, most areas of Hebei province and a
118 part of Shanxi province in North Plain China (NPC). A sub-catchment of it running
119 through Beijing, Langfang (Hebei province) and Tianjin was studied in this study
120 (Fig. 1), where around 70% of population (> 26 million capita) in Beijing and Tianjin
121 reside. The study area includes Wenyu River (length, 48 km), Beiyun River (42 km),
122 Haihe River (73 km) and Yongdingxin River (66 km). It receives the untreated
123 wastewater around this area and the effluent from wastewater treatment plants
124 (WWTPs) connected to a predominant proportion of population in Beijing and
125 Tianjin.
126

Fig. 1. The study sub-catchment and the location of sampling sites in the Haihe River basin

The sampling campaign was conducted during the dry season in late October 2016. There was no rainfall during the sampling period and the average temperature was about 10 ℃. Water samples from 51 sites (Fig. 1) were collected. Station S1 was located at the Shahe reservoir outfall. Stations S2, S5 and S10 were located at the outfalls of UW sewers. Stations S7, S13, S16, S20, S42 and S47 were located at the WWTP discharge points. The first four WWTPs were the top four largest WWTPs in Beijing and afford the treatment of ca. 60% of wastewater treated by all WWTPs in Beijing. WWTP6 (S47) is among the largest WWTPs in Tianjin. More details on WWTPs are given in Table S1 in the Supporting Information (SI). The grab surface water (0-20 cm) samples were collected into pre-cleaned amber glass bottles, acidified to pH=2.5 by using 2 M HCl and stored in iceboxes during transport to the laboratory. They were stored at 4 °C in the fridge in the laboratory and pretreated within 24 hours. The river flow rate (m^3/s) and flow velocity (m/s) for each sampling site were measured with a Flow Tracker ADV instrument (SonTek, USA).

2.2 Standards and reagents

The target chemicals include five preservatives (four parabens and one precursor), three disinfectants and one antioxidant, which are *p*-hydroxybenzoic acid (PHBA), methylparaben (MEP), ethylparaben (ETP), propylparaben (PRP) and butylparaben (BUP), TCC, TCS and *ortho*-phenylphenol (OPP), butylated hydroxyanisole (BHA). The properties of the studied compounds are provided in SI Table S2. *p*-

Hydroxybenzoic-2,3,5,6-d_4 acid (PHBA-d_4), methyl 4-hydroxybenzoate-ring-$^{13}C_6$ (MEP-^{13}C), ethyl 4-hydroxybenzoate-ring-$^{13}C_6$ (ETP-^{13}C), propyl 4-hydroxybenzoate-ring-$^{13}C_6$ (PRP-^{13}C), butyl 4-hydroxybenzoate-ring-$^{13}C_6$ (BUP-^{13}C), triclosan-d_3 (TCS-d_3), 2-phenyl-$^{13}C_6$-phenol (OPP-^{13}C) and butylated hydroxyanisole (methoxyl-d_3) (BHA-d_3) were used as internal standards (ISs) and were obtained from Sigma-Aldrich (UK) and QMX Laboratories (UK) with the purity ≥ 97%.

2.3. Sample extraction and analysis

The method of the sample pretreatment and extraction mainly referred to previous studies (Chen et al., 2016a; Chen et al., 2017). In short, the water sample (1 L) was filtered through 0.7 μm glass microfiber filters to remove suspended particles and then spiked with mixed ISs (100 ng each IS). Filtered samples were extracted by the reversed-phase Oasis HLB solid-phase extraction (SPE) cartridge (200 mg, 6 mL, Waters Corporation, Milford, MA, USA). The final extract was concentrated to 1 mL, followed by syringe filtration (0.22 μm, PTFE, Whatman, USA) and transferred to 2 mL amber vials for storage at -18 °C before analysis. Triplicate samples were conducted for each sampling site. Detailed information on reagents and pretreatment is in SI. The UPLC-ESI-MS/MS (ultra-high-performance liquid chromatography (LC-20ADXR, Shimadzu, Kyoto, Japan) -electrospray ionization tandem mass spectrometer (AB Sciex API 4500, Applied Biosystems, Foster City, CA, USA)) was employed to detect the target chemicals in water samples. It was performed in the negative multiple reaction monitoring (MRM) model with unit mass resolution. The LC system was equipped with a Waters Xbridge BEH-C18 XP column (particle size

2.5 μm, 2.1 mm × 100 mm), which had a pre-column (2.5 μm, 2.1 mm × 5 mm) for chemical separation. The detailed instrumental setting for chemical detection is in SI Table S3 and Fig. S1.

2.4 Quality assurance and quality control

Method accuracy and system performance were checked by conducting spiked experiments in river and tap water. The recovery of the analytical method ranged 69.8-93.7% for river water and 78.1-106% for tap water, respectively (Table S4). Reagent blanks were also analyzed with samples and the calculated method quantification limit (MQL) and detection limit (MDL) are given in Table S5 of SI. The relative standard deviations (RSDs) of the triplicate samples for individual sites were less than 15%.

2.5 Backward calculation of daily human exposure

In this study, the backward-calculation method was introduced to estimate the daily human exposure to HPCPs. The method is described as follows. The chemical loading mass per capita (mg/day/cap) in the influent to each WWTP was backward calculated by Eq. 1.

$$\text{Loading\_Mass}_{backward} = \frac{E}{(1-R)\times P} \quad (1)$$

where E (mg/day), R (-) and P (capita) are the chemical emission from WWTP effluents, removal efficiency in WWTPs and the population served by respective WWTPs. The emission of individual chemicals from the WWTPs was estimated by multiplying chemical concentrations in WWTP effluents and discharge flow rates of

effluents. As the measured discharge flow rate was instantaneous, the designed maximum daily treatment capacity of WWTPs was used to calibrate the discharge duration within a day if the measured discharge flow rate is greater than the theoretical average discharge rates within 24 hours based on the designed daily treatment capacity. Measured removal efficiencies of the four parabens, TCS and TCC in WWTPs were collected from the literature. They were in the range of 63-99% (mean in brackets, 94%), 75-96% (90%), 64-98% (88%), 71-99% (96%), 35-99% (71%) and 20-98% (61%) for MEP, ETP, PRP, BUP, TCS and TCC, respectively (Agüera et al., 2003; Anumol et al., 2016; Bendz et al., 2005; Bester, 2003; Chen et al., 2018; Heidler and Halden, 2008; Lozano et al., 2013; Wang and Kannan, 2016; Ying and Kookana, 2007). The population served by each WWTP is shown in Table S1.

2.6 Forward calculation of the chemical usage

A forward calculation of the mass loading to WWTPs for four parabens, TCS and TCC was conducted by compiling the data derived from a market survey on the usage of the six chemicals in food, pharmaceuticals and consumer products. The human exposure pathways of parabens mainly contain the oral ingestion from the foodstuff and pharmaceuticals (as excipients) and the dermal exposure by the external use of consumer products. Meanwhile, TCS and TCC are only used externally with consumer products. The usage and excretion of the four parabens from the ingested foodstuff or pharmaceuticals were estimated by Eqs. 2 and 3, respectively.

$$Usage_{Ing.} = EDI \times BW \quad (2)$$

$$\text{Excretion} = \text{Usage}_{\text{Ing.}} \times \varepsilon \quad (3)$$

Where $\text{Usage}_{\text{Ing.}}$ (mg/day/cap) is the amount of parabens daily ingested per capita. EDI (mg/kg bw/day) indicates the estimated daily intake of chemicals per weight and BW refers to body weights. Excretion (mg/day/cap) is the excretion of parabens per capita, which would be the input load of parabens to WWTPs. ε indicates the human excretion rate of parabens, which is around 80% (Wang et al., 2013). The value of EDI was collated from the literature. The EDI of MEP, ETP, PRP and BUP from foodstuffs was determined to be 713, 526, 128 and 23 ng/kg bw/day for Chinese based on a survey of paraben contents in 13 categories of food samples in China by a previous study (Liao et al., 2013a). The median EDI of parabens from pharmaceuticals was reported for male, female and children in China based on the measured paraben concentration in commonly used commercial pharmaceuticals in China by a previous study (Ma et al., 2016). An average value in China of the median EDIs from pharmaceuticals for different population groups was taken as 2.48, 0.97 and 0.72 ng/kg bw/day for MEP, ETP and PRP respectively. The EDI of BUP from pharmaceuticals was assumed to be 0, as it is extremely low and was not provided by Ma et al. (Ma et al., 2016). The estimated average body weight of Chinese between the age of 15-70 was 63.5 kg (CNSTATS, 2016; GASC, 2015).

The usage of parabens, TCS and TCC in consumer products was calculated as Eq. 4.

$$\text{Usage}_{\text{Dermal}} = \frac{\sum_i T_i \times F_i \times I_i}{365 \times P} \quad (4)$$

where $\text{Usage}_{\text{Dermal}}$ (mg/day/cap) indicates the amount of chemicals for external use.

i indicates different HPCP categories such as shampoo, face and body care; T_i, F_i and I_i indicate the amount of products sold in the Chinese market annually (mg), the fraction (-) of product variants containing the chemical and the inclusion level (-) of chemicals for product category i. T_i for the Chinese market was from the Euromonitor database (Euromonitor, 2015). It was spatially interpolated by GDP to obtain the T_i for the Beijing-Tianjin market. F_i and I_i of parabens were estimated based on the survey of detection frequency and concentrations of these chemicals in HPCPs in Tianjin by Guo et al. (Guo et al., 2014), as shown in Table 1. F_i and I_i for TCS and TCC were from a previous study (Zhu et al., 2016). The sum of $\text{Usage}_{\text{Dermal}}$ and Excretion is the loading mass of chemicals to WWTPs from the forward calculation.

Table 1 The fraction (F_i) of products containing MEP, ETP, PRP and BUP and the inclusion level (I_i) in Beijing and Tianjin market

2.7 Probabilistic research

A probabilistic study was conducted on both backward-calculated mass loadings and the forward-calculated usage and mass loading of the six chemicals by Monte Carlo simulation to take account of the uncertainty of parameters relevant to above equations. For the backward calculation, the average per capita emission (E/P) and the standard deviation (STD) were acquired from the discharge of the six WWTPs. The average and STD of removal efficiencies for each chemical were estimated based on the collection from the literature (Table S6). For the forward calculation, above EDI

per weight from foodstuff and pharmaceuticals was taken as the average. Their STD was set to be 30% of the average (Escher et al., 2011). The average and STD of the per capita usage of the six chemicals in consumer products were calculated based on the different per capita usage in different counties in Beijing and Tianjin. All the value and distribution are shown in Table S6-S7. The average and STD values were used to generate random values that align the distribution. 10,000 runs were conducted for Monte Carlo simulation.

3. Results and discussions

3.1 Occurrence of HPCPs in the rivers

All nine target compounds were detected in 100% of the water samples in the sub-catchment of Haihe River (Table S8). A high detection frequency of these chemicals was also found in other catchments such as the Jiulong River (Fujian province), Pearl River, Yellow River and Yangtze River (Liu et al., 2015; Sun et al., 2016; Wang et al., 2012; Yu et al., 2011), which indicates their ubiquitous presence in China. The total concentration of the nine HPCPs ranged 555-2793 ng L^{-1} with a median of 660 ng L^{-1}. The average concentration of individual chemicals was 65.8, 101, 69.6, 88.5, 72.8, 149, 102, 102 and 77.7 ng L^{-1} for PHBA, MEP, ETP, PRP, BUP, TCC, TCS, OPP and BHA, respectively (Table S8). The coefficient of variation (CV) of the concentration varied between 38-126% (54% for ∑HPCPs) for individual chemicals, which indicated a wide spatial variation and large difference among chemicals. The spatial variation might result from the combination of distinct distances of sampling sites

279 from emission sources, the variation in discharge flow and the potential existence of
280 other emissions that were not captured. The largely different CVs among chemicals
281 might be a result of their different usage and physicochemical properties. For
282 example, they may be released with a varied composition along the river due to
283 different usage patterns; and their different degradation rates and octanol-water
284 partition coefficient (K_{ow}) may lead to varied attenuation rates in water along the river.
285 However, the concentration was generally at a level of ng L^{-1} for individual chemicals
286 (Table S8).

287 Generally, the detected concentration in river waters in this study was at a moderate
288 level compared to those from other studies in Asia, Europe, North America (NA) and
289 Africa (Table S9). The concentration of TCS and TCC measured in Haihe River in
290 Tianjin by Zhao et al. during 2007-2009 (Zhao et al., 2013) was lower than that in this
291 study. The rivers in Asia had a higher concentration of parabens, TCS and TCC than
292 those in most studies in Europe and NA. The exception was the concentration of TCC
293 in urban streams in Great Baltimore, USA sampled during 2002-2003, and TCS in
294 139 streams in USA sampled during 1999-2000, Lake Greifensee, Switzerland
295 sampled in 1999 and Llobregat River, Spain sampled in 2007 (Halden and Paull,
296 2004; Kolpin et al., 2002; Singer et al., 2002; Kantiani et al., 2008), which was
297 extremely high. The samples of these studies were all measured about a decade ago.
298 Because products that contained parabens are mostly produced in China or India and
299 then imported by Europe, the release from manufacturers in China could be an
300 important source.

Few studies have reported data on PHBA, OPP and BHA in surface water. Li et al. (2016) reported a higher PHBA concentration (mean, 239 ng L^{-1}) but lower paraben concentrations in rivers and lakes in Beijing compared to this study. It is possible that the transformation efficiency of parabens to PHBA was higher in their study than in this study. However, Haman et al. clarified that the large transformation of parabens to PHBA due to hydrolysis is unlikely in aquatic environment, as the river water pH range is normally lower than the pKa of parabens (pKa, 8.2-8.5) (Haman et al., 2015). Li et al. conducted monthly gauging campaigns within a year during 2013-2014, which reflected an annual average (Li et al., 2016). The possibility of unnormal situation for a whole year was probably low. Therefore, the difference in the two studies was possibly a result of distinct sources in corresponding sampling periods between the two studies.

3.2 Spatial distribution of HPCPs along the river

Fig. 2. Total concentration of the nine HPCPs (ng L^{-1}) for each sampling site along the river; sites with '*' indicate the effluent from the wastewater treatment plants (WWTPs); UW indicates untreated wastewater discharges; Pie charts show the composition of HPCPs

The outfall of Shahe Reservoir (S1) had the lowest ∑HPCPs concentration along the sub-catchment. Two UW discharge sites along the Wenyu River within Beijing, i.e. S2 (2793 ng L^{-1}) and S10 (2571 ng L^{-1}), had the highest ∑HPCPs concentrations (Fig. 2) among all sites. Previous studies have also indicated the large release of untreated

domestic, industrial and agricultural wastewater to the Wenyu River. Furthermore, a higher concentration of organic contaminants was found in such UW than in WWTP effluents and river water samples (Chen et al., 2016b; Qiao et al., 2014). The average ∑HPCPs concentration ranged 610-704 ng L^{-1} in the Wunyun, Beiyun, Haihe and Yongdingxin Rivers (Table S10) and differences of ∑HPCPs concentrations between rivers were not found to be significant by the Tukey-Kramer HSD (honestly significant difference) test. The CV of average concentrations of ∑HPCPs for different rivers was 13%.

Fig. 3. Average concentrations of individual chemicals for samples from effluent of the wastewater treatment plants (WWTPs, grey column, n=6), samples from the untreated wastewater (UW, n=3) discharges (black column) and other river water samples (white column, n=42). The error bars represent standard deviations (STD).

The average concentration of the individual HPCPs in WWTP effluents and UW discharges was 1.3-2.2 and 1.6-7.5 times of that in river water samples, respectively (Table S10 and Fig. S2). The chemical concentration was significantly higher in UW discharges than in WWTP effluents with the exception of TCC (Fig. 3 and Fig. S3-S4). Major contributors to the high average concentration in UW discharges were sites S2 and S10 for each chemical (Fig. 2) except TCC, whilst S5 had a similar concentration level to WWTP effluents for each chemical. The concentration of TCC at S2 and S10 was even lower than that in WWTP effluents. Detailed information on the sources and types of UW at the three sites is not available to the authors. Hence, the reasons for the observed differences between WWTP effluents and UW are not

conclusive. The concentration declined significantly when WWTP effluents and UW discharges entered the mainstream due to dilution and possible degradation (Baena-Nogueras et al., 2017; Inam et al., 2015; Johnson, 2010). For river water samples, the concentration of PHBA was significantly higher in the Yongdingxin River (mean, 87 ng L^{-1}) than in the other three rivers (54-56 ng L^{-1}). The concentration of ETP and PRP was significantly higher in the Wenyu River (58 and 70 ng L^{-1} respectively) than in the Beiyun River (52 and 60 ng L^{-1}). The concentration of TCS was significantly higher in the Wenyu River (93 ng L^{-1}) than in the Haihe River (66 ng L^{-1}) and Yongdingxin River (68 ng L^{-1}). The Wenyu River (97 ng L^{-1}) had a significantly higher concentration of OPP than the Haihe River (70 ng L^{-1}). Finally, the Yongdingxin River (84 ng L^{-1}) had a significantly higher concentration of BHA than the Haihe River (55 ng L^{-1}). In general, a significant positive correlation was found between concentrations of most pairs of chemicals along the catchment, except for pairs of PHBA and most chemicals, and pairs of TCC-TCS, TCC-OPP (Table S11). This implies similar sources of origin for most of these chemicals in the catchment (Kimura et al., 2014; Li et al., 2016). The exception possibly resulted from chemical properties and different sources. For example, natural sources such as green plants could release PHBA, whilst it is also a metabolite of parabens (McQualter et al., 2005).

3.3 Composition of HPCPs in the river

The paired-sample T Test indicated that the three disinfectants (OPP, TCS and TCC) exhibited significantly higher concentrations than other chemicals. For more than

370 80% of the sampling sites, the three chemicals contributed over 40% of the ∑HPCPs
371 concentration. Generally, the concentration of TCC (range, 76.7-317 ng L^{-1}) was the
372 highest amongst all targeted chemicals in this catchment, which contributed 6% to
373 28% of the ∑HPCPs concentration with an average of 19%. This might have been a
374 result of the wide use of these chemicals in HPCPs compared to other targeted
375 chemicals (Zhao et al., 2013; Zhu et al., 2016). The abundance of MEP (54.7-810 ng
376 L^{-1}) and PRP (43.5-627 ng L^{-1}) followed that of the disinfectants in this sub-
377 catchment, accounting for 11% and 10% of the ∑HPCPs concentration, respectively.
378 They have been found to be the most abundant parabens in raw wastewater by many
379 researchers (Haman et al., 2015). Previous studies found a higher inclusion level of
380 MEP than the other three parabens in HPCPs and foodstuffs in China (Guo et al.,
381 2014; Liao et al., 2013a). On average, PHBA and ETP contributed 8.0% and 8.4% of
382 the ∑HPCPs concentration, respectively, which were the smallest percentages among
383 all chemicals.

384 The composition of HPCPs in river water samples was relatively constant with the
385 following exceptions: the proportion of PHBA and parabens was slightly higher in the
386 Haihe River and Yongdingxin River in Tianjin compared to the Wenyu River and
387 Beiyun River in Beijing. This aligned the difference of the HPCP composition in
388 WWTP effluents in Beijing and Tianjin (Fig. S5-S6), indicating probably different
389 consumption patterns of these chemicals in the two areas. In contrast, the proportion
390 of MEP and PRP in UW discharges at S2 and S10 was much higher than that in other
391 samples, which resulted in a significantly different composition of HPCPs (Fig. S6). It

392 also possibly implied the potential release of parabens from the manufacturer close to
393 the two sites.

394

395 **Fig. 4.** A. Mass flux of ∑HPCPs (g/hr) of the river/discharge cross section for each
396 sampling site along the river; sites with '*' indicate the effluent from wastewater
397 treatment plants (WWTPs); UW indicates untreated wastewater; B. the specific value
398 of HPCP fluxes in WWTP effluents, UW discharges, at connection points of two
399 rivers and estuaries of the Yongdingxin River and Haihe River to Bohai Bay; the
400 values in brackets are mass fluxes (g/hr) of ∑HPCPs, ∑parabens (inclusive of MEP,
401 PRP, ETP and BUP), ∑disinfectants (inclusive of TCS, TCC and OPP) and BHA in
402 sequence.

403

404 *3.4 Mass fluxes of HPCPs along rivers*

405 Due to the influence of the variation in river flows, the mass flux rather than the
406 concentration of HPCPs might facilitate an understanding of the change of HPCP
407 loadings and emissions along the river (Johnson, 2010). Fig. 4 shows the spatial
408 variation of the mass flux of ∑HPCPs along the basin, which gradually increases from
409 upstream (Wenyu River) of the catchment to downstream (Haihe River and
410 Yongdingxin River). ∑HPCPs mass fluxes increased from 8.7 g/hr to 38 g/hr along
411 the Wenyu River with an average of 21 g/hr. The spatial variation (CV, 32-48%) of the
412 mass flux and its difference between the starting and the end points (2.3-9.7 times of
413 difference) of the Wenyu River for individual chemicals were the largest amongst all
414 rivers (Table S12). This pattern possibly resulted from a 'cleaner' source at the outfall
415 of the Shahe Reservoir and the input of wastewater from Beijing. The mass flux
416 increased relatively slowly along the Beiyun River but more significantly from the
417 beginning of the Haihe River and the Yongdingxin River in east Tianjin. The rapid

418 increase could be attributed to the local release from WWTP effluents and factories or
419 possibly the input from tributaries, such as the Chaobaixin River. The loading of
420 ∑HPCPs to Bohai Bay at the estuary of the Haihe River and the Yongdingxin River
421 was about 181 g/hr and 214 g/hr, respectively.

422 Significant attenuation of HPCPs with the river flow was observed based on mass
423 balance (Fig. 4B). Based on the chemical concentration and the discharge rate, the
424 loading of ∑HPCPs into the Wenyu River was estimated to be 133 g/hr from the three
425 WWTPs and 23 g/hr from the three UW discharges. The total loading of ∑HPCPs
426 along the Wenyu River should be over 175 g/hr cumulatively taking account of the
427 release from the Shahe Reservoir and the input from the Lingou River. Therefore,
428 conservatively, at least 79% of the mass of the dissolved ∑HPCPs was lost with an
429 estimated range of 59-85% for individual HPCPs (Table S12). The loss could be
430 attributed to degradation, adsorption to suspended particles or sediment and possible
431 abstraction of the river water (Liao et al., 2013b). Fig. 4 illustrates that WWTP
432 effluents contributed more HPCP loadings to the river than UW discharges, although
433 UW discharges have higher concentrations of chemicals but lower discharge flows.
434 However, previous studies clarified that UW discharges cannot be ignored. For
435 example, about 1.37 out of 1.52 billion tonnes wastewater in Beijing can be treated
436 (CNSTATS, 2016; MEP, 2015; Wang et al., 2015). About 0.4 million tonnes UW
437 might be discharged to the city river network diffusively every day in Beijing but this
438 is not easily captured.

439 *3.5 Estimation of human exposure and WWTP loadings*

440 To facilitate an understanding of human exposure to these chemicals and to support
441 chemical management in the target region, results from the backward calculation and
442 forward calculation were compared. The backward-calculated average loading to
443 WWTPs with influents was 2.0 (range, 0.033-302 mg/day/cap), 1.1 (0.044-6.2), 1.0
444 (0.027-13), 3.0 (0.049-2491), 0.51 (0.031-3527) and 0.61 (0.033-28) mg/day/cap for
445 MEP, ETP, PRP, BUP, TCS and TCC respectively in Beijing-Tianjin region. The range
446 in brackets considered the uncertainty of the chemical removal efficiency in WWTPs
447 and the different per capita emission among the six WWTPs (Table S6-S7). The
448 estimated loading and the range for different WWTPs are provided in Table S13-S14.
449 The per capita loading and emission were the highest in WWTP1 in Beijing and
450 WWTP5 in Tianjin.

451 By the forward calculation, the exposure level via different exposure pathways and
452 the total exposure level are provided in Table 2. Dermal exposure by using consumer
453 products was estimated to be the predominant exposure pathway for MEP, PRP and
454 BUP (78-91%). Oral exposure via foodstuffs was estimated to be the major exposure
455 pathway for ETP (72%). Taking account of the human excretion rate of parabens, the
456 forward-calculated average loading to WWTPs was 0.49, 0.04, 0.28, 0.006, 0.51 and
457 0.22 mg/day/cap for MEP, ETP, PRP, BUP, TCS and TCC in this region. They were
458 extremely close to the backward-calculated average loading of TCS and TCC, but 1-3
459 orders of magnitude lower than that of parabens. However, they were within the range
460 of the loading from the backward calculation with the exception of BUP. The forward-

461 calculated daily loading of parabens to WWTPs was only slightly lower than the
462 forward-calculated human exposure level due to the generally low proportion of oral
463 intake of these chemicals.

464

465 **Table 2** The EDI of chemicals from foodstuffs and pharmaceuticals and estimated
466 usage of chemicals contained in HPCPs (mg/day/cap) by the forward calculation from
467 the market survey; '-' indicates no intake from foodstuff and pharmaceuticals
468

469 The result from the probabilistic study is shown in Fig. 5 and Fig. S7. The estimated
470 loading to WWTPs from the backward calculation covered a much wider range than
471 the forward-calculated loading, which reflects the great influence from the uncertainty
472 of the chemical removal efficiency in WWTPs. The mass loading of ∑parabens from
473 the backward calculation was significantly higher than that from the forward
474 calculation. The median backward-calculated mass loading of ∑parabens was ca. 6.7
475 mg/day/cap from the probabilistic study. The median forward-calculated usage and
476 loading of ∑parabens to WWTPs were approximately 0.83 and 0.81 mg/day/cap,
477 respectively. The backward-calculated mass loading for TCC and TCS was much
478 closer to the forward estimated usage especially for TCS (Fig. S7). The median
479 backward-calculated mass loading and forward-calculated usage were 0.42 and 0.51
480 mg/day/cap respectively for TCS and 0.51 and 0.22 mg/day/cap respectively for TCC.
481

482 **Fig. 5**. Histogram of probabilistic ∑paraben4 mass loadings from the backward
483 calculation (blue) and forward calculation (green); and the ∑paraben4 usage (red) by
484 the forward calculation.
485

The difference between the two methods of calculation may result from several uncertainties: (1) The forward calculation of the usage or mass loading of parabens to WWTPs might be underestimated due to the lack of complete market data of consumer products or daily exposure levels through the intake of foodstuffs and pharmaceuticals available. The closer estimation from the two calculation methods for TCS and TCC probably has demonstrated this, as the forward calculation for the two chemicals derive from our previous studies, which processed more complete market data (Zhu et al., 2018; Zhu et al., 2016). (2) The existence of industrial emissions from factories in this region was highly probable. Their release to WWTPs is probably captured in the measurement in this study and included in the backward calculation, which would not be used by local population. (3) The chemical removal efficiency was possibly overestimated. As the current removal efficiency for these chemicals was not measured for the six WWTPs, there is a possibility that the chemicals were not properly removed with expected removal efficiencies collected from the literature. (4) The backward calculation was only based on one monitoring campaign in the dry season. The usage of some HPCPs might be distinct in different seasons. Meanwhile, the market data or survey for the forward calculation may reflect an annual average consumption. (5) The grab sample possibly reflects an instantaneous situation, which cannot consider the variability over time. These reasons may cause the discrepancy of mass loadings to WWTPs by the two calculation methods for most of the six chemicals.

4 Conclusions

This study determined four parabens, OPP and BHA in the sub-catchment of the Haihe River basin, which has filled the data gap for these pollutants especially in the target region. The concentration of the nine HPCPs was at a level of ng L^{-1} in this region. A backward calculation method has been introduced to trace back potential human exposure levels and mass loadings to WWTPs from the measurement of the target HPCPs in WWTP effluents. The discrepancy of the result for parabens from this method and the forward calculation may indicate a current industrial release of these chemicals in the target region or the underestimation of the usage from the incomplete market data and paraben contents in consumer products provided by previous studies. This indicates that a more accurate estimation of the usage and more monitoring campaigns for investigating chemical sources are required. The method of the backward calculation is extremely different from the forward-calculation method that is commonly used. It could provide information from a different aspect. This is a potential method to support the control of contaminants in aquatic environment and the management of human consumptions of chemicals.

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Appendix A. Supplementary material

Supplementary data to this article can be found online.

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