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Multimedia fate modeling and risk assessment of a commonly used azole fungicide climbazole at the river basin scale in China

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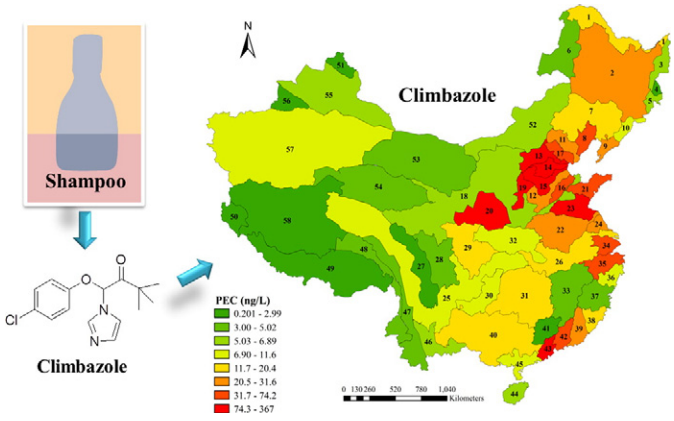
HIGHLIGHTS

- Emission of climbazole in the whole China was estimated based on market research data.
- Level-III fugacity model used to predict the fate of this chemical at the basin scale
- The mass inventory in the whole China: 294 t, with 6.79% in water and 83.7% in sediment
- High aquatic risks posed by climbazole expected in 2 out of 58 basins in China

GRAPHICAL ABSTRACT



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ABSTRACT

Climbazole is an antidandruff active ingredient commonly used in personal care products, but little is known about its environmental fate. The aim of this study was to evaluate the fate of climbazole in water, sediment, soil and air compartments of the whole China by using a level III multimedia fugacity model. The usage of climbazole was calculated to be 345 t in the whole China according to the market research data, and after wastewater treatment a total emission of 245 t was discharged into the receiving environment with approximately 93% into the water compartment and 7% into the soil compartment. The developed fugacity model was successfully applied to estimate the contamination levels and mass inventories of climbazole in various environmental compartments of the river basins in China. The predicted environmental concentration ranges of climbazole were: 0.20–367 ng/L in water, and 0.009–25.2 ng/g dry weight in sediment. The highest concentration was mainly found in Haihe River basin and the lowest was in basins of Tibet and Xinjiang regions. The mass inventory of climbazole in the whole China was estimated to be 294 t, with 6.79% in water, 83.7% in sediment, 9.49% in soil, and 0.002% in air. Preliminary risk assessment showed high risks in sediment posed by climbazole in 2 out of 58 basins in China. The medium risks in water and sediment were mostly concentrated in north China. To the best of our knowledge, it is the first report on the emissions and multimedia fate of climbazole in the river basins of the whole China.

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1. Introduction

Personal care products (PCPs), including moisturizers, lipsticks, shampoos, hair colors, deodorants and toothpastes, are widely used to improve the quality of human life (Boxall et al., 2012). A large variety of active ingredients in PCPs are considered as "emerging pollutants", and they are often high production volume chemicals (Daughton and Ternes, 1999; Boxall et al., 2012). After use, these chemicals are released directly or indirectly through wastewater treatment plants (WWTPs) into the receiving environments (Ternes et al., 2004). Therefore, it is essential to understand their fate and risks in the environment.

Climbazole is an azole fungicide used as an antidandruff ingredient in some household and personal care products such as shampoos, with its content up to a maximum concentration of 2.0% in formulations (SCCP, 2009). It is reported that the usage of this chemical in the European Union is in the range of 100 to 1000 tons per annum (Perez-Rivera et al., 2009). Due to incomplete removals in WWTPs (Wick et al., 2010; Chen et al., 2012), climbazole could enter into aquatic and terrestrial environments via sewage effluent discharge and sludge application. As the result, climbazole as well as other azole fungicides were detected in various environmental media such as effluent, sludge, surface water and sediment as well as soil (Kahle et al., 2008; Huang et al., 2010; Stamatis et al., 2010; Peng et al., 2012; Wick et al., 2010; Chen et al., 2012, 2014). Climbazole was reported to be quite toxic to aquatic organisms (Richter et al., 2013). In fact, azole fungicides showed potential endocrine disrupting effects to aquatic organisms due to their disturbing action on CYP450-regulated steroidogenesis (Kahle et al., 2008; Ankley et al., 2005; Kjærstad et al., 2010).

Nevertheless, measured concentrations of climbazole and other azole fungicides in the environment are still very limited worldwide. There are 58 basins in China with more than 1500 rivers (Statistical Yearbook of China in 2011). Monitoring campaigns for climbazole, however, have only been conducted in three rivers with a few samplings (Chen et al., 2014; Heeb et al., 2012; Qi et al., 2014). Modeling approach can provide an alternate method to estimate the environmental concentrations of this chemical. And it can be a time-saving and less expensive operation for a large scale assessment. Some studies have demonstrated that by coupling of chemical usage data, population, removal rate in WWTPs, and a parameterized multimedia model describing the fate of chemicals, the environmental exposure concentrations of ingredients used in PCPs can be predicted (Keller et al., 2007; Price et al., 2009, 2010a, 2010b; Whelan et al., 2012). Multimedia fugacity models are well established, well documented and widely used for predicting the environmental fate of chemicals at various scales by numerous researchers (single river scale, regional scale, and global scale) (Cao et al., 2004; Mackay, 2001; Prevedouros et al., 2004; Tan et al., 2007; Tao et al., 2003; Wang et al., 2012). In addition, successful modeling was reported for some PCPs such as triclosan based on their chemical usage data and level III fugacity model in our previous studies (Zhang et al., 2013; Zhao et al., 2013), as well as for natural steroids in all basins of the whole China (Zhang et al., 2014).

The aim of this study was to predict and evaluate the environmental concentrations and multimedia fate of climbazole at the river basin scale in the whole China using a level III multimedia fugacity model. Market research data was collected for the estimation of climbazole usage. A sensitivity analysis was performed to identify the most influential parameters and processes responsible for the fate of chemicals, while an uncertainty analysis with Monte Carlo calculation was used to estimate the total variance associated with the model outcome. Environmental risks were also assessed based on the simulated concentrations and literature ecotoxicity data by using the risk quotient (RQ) approach. The results can help to understand the contamination profiles of climbazole and mitigation of its potential risks in Chinese riverine environments.

2. Methodology

2.1. Basic basin unit in China

According to the Industry Standard of China (ISC, 2000), the whole China is divided into 58 basins (all the secondary rivers are included). To simplify the model description, an ID was allocated to each basin (Fig. 1) and the detailed basin information is displayed in Table S1 (Supplementary information). The geographic information layers of the basin system and administrative region of China are both available at the National Geomatics Center of China (http://sms.webmap.cn/). The map of China basins was created by ArcGIS 9.3 software. Details about administrative areas contained in each basin are displayed in the Supplementary information (SI-A). And the national wide multimedia modeling for climbazole was conducted in the unit of each basin.

2.2. Estimation of climbazole emissions

Climbazole is widely used as an antidandruff active ingredient in hair care formulations with a maximum concentration of 2.0% (SCCP, 2009). The method used to estimate consumption of climbazole was based on the market sales data for hair care products taken from Euromonitor (www.euromonitor.com). Meanwhile, the Mintel's Global New Products Database (GNPD) (www.gnpd.com) provided the ingredient lists associated with shampoo products released to the Chinese market in 2011. Consequently, with the information of market research data and ingredient list of hair care products and the inclusion level defined for climbazole in hair care formulations, we were able to estimate the total amount of climbazole consumed in the whole China. As some studies available in literature have demonstrated that the emission of chemical ingredients included in the personal care products in a region corresponded well with the *per capita* chemical consumption (PCC) estimate (mg/cap/yr) inputs and populations (Holt et al., 1998; Price et al., 2009; Whelan et al., 2012), we assumed that climbazole was uniformly distributed based on the population in China. The emission rate for each of the 58 basins was calculated according to the average consumption data *per capita* and the populations in the region. The detailed data sets of the populations for all of the 58 basins are available in the Supplementary information (SI-A).

After use, the chemical ingredient associated with the products is discharged directly or indirectly into the environment. But for the climbazole from urban population, the chemical mass is partly removed in WWTPs before discharge into the receiving environments in China (Chen et al., 2012), while for that from rural population, it is mostly discharged directly into the environment due to the low sewage treatment rate in majority of rural areas in China (GOSC, 2012). The climbazole emissions from the urban population were calculated based on the local wastewater treatment rate (SI-A), the removal efficiency of the target chemical in WWTPs (Table 2) and the corresponding usage of climbazole from the urban population. And for the emissions from the rural population, the usage of climbazole equals to the emission to the receiving environment. Thus, the emission to the receiving environment includes three parts: emission from the rural population, emission from the urban population without WWTPs (direct discharge), and emission from WWTPs (indirect discharge). Wastewaters whether treated or untreated are mainly received by the aquatic environment. In addition, sewage irrigation and sludge application are other pathways for the chemical to reach the soil environment. But in China, disposal of sewage sludge on agricultural land is still prohibited (Chen et al., 2013). The ratio of sewage irrigation area to the whole agricultural land was 6.65% according to the second national survey of sewage irrigation (Fang, 2011). Assuming that the irrigation water amount per unit area of the agricultural land was the same, the chemical emission into the soil compartment via sewage irrigation can be estimated by the ratio of the sewage irrigation volume to the sewage wastewater discharge volume multiplied by the chemical emission from the sewage wastewater. The detailed equations for the

Fig. 1. Map of China basin. ID codes are given on the map.

estimation of climbazole emissions can be found in the Supplementary information (SI-A and SI-B).

2.3. Multimedia model description

A level III fugacity model based on the approach of Mackay and Paterson (1991) was applied to predict the multimedia fate of climbazole at the basin scale in the whole China. The model includes 4 bulk compartments and 10 sub-compartments: air (air, particulates), water (water, suspended solids, and fish), soil (air, water and solids) and sediment (water and solids). The environmental processes expressed by transfer fluxes in the model include: emissions, advective flows, degrading reactions, and interphase transport by diffusive and non-diffusive processes. Under the steady-state conditions the total input fluxes from the individual compartments equal to the output fluxes, and the mass balance equation is established in terms of transfer fluxes for the 4 bulk compartments:

$$T_{01t} + T_{21d} + T_{31d} = T_{10t} + T_{12d} + T_{12p} + T_{12w} + T_{13d} + T_{13p} + T_{13w} + T_{10m},$$
$$T_{02t} + T_{02h} + T_{12d} + T_{12p} + T_{12w} + T_{32e} + T_{32l} + T_{42d} + T_{42r} = T_{20t} + T_{21d} + T_{24d} + T_{24s} + T_{20m} + T_{2f},$$
$$T_{13d} + T_{13p} + T_{13w} + T_{23h} = T_{30m} + T_{31d} + T_{32e} + T_{321},$$
$$T_{24d} + T_{24s} = T_{40m} + T_{42d} + T_{42r}.$$

The transfer fluxes (T_{ijk}) (mol/h) could be calculated as $D_{ijk}f_i$, where D_{ijk} is a transfer coefficient with unit of mol/(h · Pa), and f_i is the fugacity of the compartment with the unit of Pa. The definition of the transfer processes and the corresponding D_{ijk} value calculation method are listed in Table 1.

As shown in Table 1, the transfer coefficients (D_{ijk}) for different environmental media and processes can be calculated by using various functions relating to the parameters. These included 14 parameters describing the physicochemical properties of climbazole (Table 2) and 42 parameters describing the environment (SI-B, Tables S2–S3). Some of the environmental parameters were taken from the default value of Mackay and Paterson (1991), and applied to all 58 basins (Table S2). Parameters about physical and chemical properties of climbazole were also applied to all the basins (Table 2). The rest of parameters, such as water area (A_2), depth (h_1, h_2, h_3, h_4) and organic carbon content of each compartments (O_{23}, O_{33}, O_{43}), were the site-specific data from the published papers or reports (Table S3). We collected values for each parameter from the published literature or reports. And if more than one value were collected, the average value was selected to solve the model equations. Of the parameters, the Henry's law constant (H), vapor pressure (P_S) and half-lives of the chemical in air (t_1), water (t_2) and soil (t_3) compartment are the typical temperature-dependent variables and were calculated with temperature corrections according to Vidal (2003), Mackay et al. (2006) and Saltveit (2004). With the relating equations (Supplementary information, Eqs. 4–8) for the relationships between the temperatures and those parameters, we can get those parameters at different temperature levels. More information about the parameters and the calculation method for temperature corrections and mass inventories of climbazole in each basin is described in the Supplementary information (SI-B).

To identify the most influential parameters and processes responsible for the fate of chemicals, a sensitivity analysis was applied by comparing predicted results without any changed variable with those

Table 1
Transfer processes and corresponding *D* values.

Symbol (mol/h)	Transfer process	Related *D* value (mol/h · Pa)	Fugacity multiplied (Pa)
T_{10t}	Advective flows out of the area through air	$Q_{10t} \times Z_1$[a]	f_1
T_{01t}	Advective flows in the area through air	–	–
T_{20t}	Advective flows out of the area through water	$Q_{20t} \times Z_2$[a]	f_2
T_{02t}	Advective flows in the area through water	–	–
T_{02h}	Chemical entering water from human	–	–
T_{23h}	Chemical entering soil during wastewater irrigation	–	–
T_{12d}	Diffusion from air to water	$A_2 / (1 / (K_{12} \times Z_{11}) + 1 / (K_{21} \times Z_{22}))$	f_1
T_{21d}	Diffusion from water to air	$A_2/(1 / (K_{12} \times Z_{11}) + 1 / (K_{21} \times Z_{22}))$	f_2
T_{13d}	Diffusion from air to soil	$A_3/(1 / (K_{13} \times Z_{11}) + L_3 / (B_1 \times Z_{11} + B_2 \times Z_{22}))$	f_1
T_{31d}	Diffusion from soil to air	$A_3/(1 / (K_{13} \times Z_{11}) + L_3 / (B_1 \times Z_{11} + B_2 \times Z_{22}))$	f_3
T_{24d}	Diffusion from water to sediment	$A_4/(1 / (K_{24} \times Z_{22}) + L_4 / (B_4 \times Z_{22}))$	f_2
T_{42d}	Diffusion from sediment to water	$A_4/(1 / (K_{24} \times Z_{22}) + L_4 / (B_4 \times Z_{22}))$	f_4
T_{12p}	Dry deposition from air to water	$A_2 \times K_p \times X_{13} \times Z_{13}$	f_1
T_{12w}	Wet deposition from air to water	$A_2 \times K_w \times S_c \times X_{13} \times Z_{13}$	f_1
T_{13p}	Dry deposition from air to soil	$A_3 \times K_p \times X_{13} \times Z_{13}$	f_1
T_{13w}	Wet deposition from air to soil	$A_3 \times K_w \times S_c \times X_{13} \times Z_{13}$	f_1
T_{24s}	Sedimentation	$A_4 \times K_s \times Z_{23}$	f_2
T_{42r}	Resuspension	$A_4 \times K_r \times Z_{43}$	f_4
T_{32e}	Soil particle erosion to water	$A_3 \times K_e \times Z_{33}$	f_3
T_{32l}	Soil water runoff	$A_3 \times K_l \times Z_{22}$	f_3
T_{2f}	Bioaccumulation in fish	$Y_f \times Z_{2f}/\rho_f$	f_2
T_{10m}	Degradation in air	$K_{m1} \times A_1 \times h_1 \times Z_1$	f_1
T_{20m}	Degradation in water	$K_{m2} \times A_2 \times h_2 \times (Z_2 - X_{2f} \times Z_{2f})$	f_2
T_{30m}	Degradation in soil	$K_{m3} \times A_3 \times h_3 \times Z_3$	f_3
T_{40m}	Degradation in sediment	$K_{m4} \times A_4 \times h_4 \times Z_4$	f_4

Subscripts 1,2,3,4 refer to four bulk compartments: air, water, soil and sediment, respectively.
Subscripts t, h, d, p, w, s, r, e, l, m and f refer to advective flow, human activities, diffusive, dry and wet precipitation, sedimentation, resuspension, erosion as solid and water, degradation and fish accumulation, respectively.
[a] Z_1 refers to the total fugacity capacity of air, which is equal to "$Z_{11} + Z_{13} \times X_{13}$"; and Z_2 is equal to "$Z_{22} + Z_{23} \times X_{23} + Z_{2f} \times X_{2f}$".

having only one variable changed by ±10%, and the result was expressed as sensitivity coefficient (C_S). Those sensitive parameters were further subject to uncertainty analysis. Both the modeled concentrations and fluxes are inherently variable, so are the input parameters (Cao et al., 2004). Since the inherent variable is hardly available with well-defined calculation methods, we always replace these variable values by a representative value such as the "average values". In addition, uncertainties in the parameters and estimates also existed. Propagation of the various sources of uncertainty to the model output was always evaluated by a Monte Carlo analysis (Luo and Yang, 2007). The simulation was run for 2000 times using a build-in function of "randn" in Matlab. The "randn" displayed each input parameter as a probability density function that defined both the range of values and the likelihood of the parameter having that value (Cao et al., 2004). In the function of "randn", the mean values and standard deviations of the parameters are important factors. For the parameters with only single value available, coefficients of variation were artificially assigned and used to derive standard deviations (SI-B, Table S4). The result of the Monte Carlo analysis was reported as 2000 values, and the difference between the third and the first quartiles (abbreviated as SQR) was used to quantify the uncertainties.

In addition, the developed model was also validated by comparing the predictions with the measured values collected from published reports. Climbazole was firstly monitored and detected in German WWTP by Wick et al. (2010), and the measured environmental concentrations (MECs) are not available in most of the basins in China excepting 13 samples in Haihe River (IDs: 13–14; Heeb et al., 2012), 1 sample in Yangtze River Downstream (ID: 26; Qi et al., 2014), and 21 samples in Dongjiang River (ID: 42; Chen et al., 2014). Fortunately, the only three available PECs were located in north China, central China and south

Table 2
Physical and chemical properties and half-lives of climbazole.

Symbol	Unit	Definition	Values	Ref.
M	g/mol	Molar mass of the chemicals	293	Richter et al. (2013), SCCP (2009)
ρ	g/ml	Bulk density of the chemical	1.32 at 20 °C	ECHA (2014)
MP	K	Melting point of the chemical	370	Richter et al. (2013), SCCP (2009), ECHA (2014)
BP	K	Boiling point of the chemical	645	EPI
H	Pa·m^3/mol	Henry's law constant	4.85×10^{-3} at 25 °C	[a]
Ps	Pa	Vapor pressure	9.60×10^{-4} at 25 °C	ECHA (2014)
WS	g/m^3	Water solubility	58 at 25 °C	ECHA (2014)
K_{OC}	L/kg	Organic carbon normalized partition coefficients	5942.9	ECHA (2014)
t_1	h	Half-life of the chemical in air	5 at 25 °C	EPI
t_2	h	Half-life of the chemical in water	672 at 22 °C	ECHA (2014)
t_3	h	Half-life of the chemical in soil	2880 at 25 °C	EPI
t_4	h	Half-life of the chemical in sediment	13,000 at 25 °C	EPI
BCF_f		Bioconcentration factors for fish in water	156	ECHA (2014)
B_2	m^2/h	Molecular diffusivity in water	3.32×10^{-7}	Wu and Gschwend (1988)[b]
B_4	m^2/h	Molecular diffusivity in sediment	6.75×10^{-8}	Wu and Gschwend (1988)
f'	%	Removal efficiency of target compounds in wastewater treatment plants	71.9	Wick et al. (2010), Chen et al. (2012)

[a] According to Henry's Law: *Ps* (Pa) = *H* (Pa·m^3/mol) × *WS* (mol/m^3); *WS* (mol/m^3) = *WS* (g/m^3) / M (g/mol).
[b] $B_2 = 0.36 \times (13.26 \times 10^{-5} / (0.001\text{^}1.14 \times \text{Vm}\text{^}0.589))$, Vm = M / ρ. $B_4 = 0.36 \times B_2 \times \theta$^1.33. In China, the porosity of the surface sediment (θ) was average as 65% (Water Resources and Sediment Bulletin in China).

Table 3
Aquatic toxicity data and PNEC value for climbazole.

Class	Specie	Effect	Exposure time (d)	Endpoint	Values (μg/L)	Ref.	PNEC (μg/L)	Comment[b]
Plant	*Lemna minor*	Biomass	7	EC10[a]	5.6	Richter et al. (2013), ECHA (2014)	0.56	PNEC = $EC10_{(Plant)}$ divided by 10
Algae	*Navicula pelliculosa*	Biomass	3	EC10	64.1	Richter et al. (2013), ECHA (2014)		
	Pseudokirchneriella subcapitata	Biomass	3	EC10	28.7	Richter et al. (2013), ECHA (2014)		
	Desmodesmus subspicatus	Biomass	3	EC10	32	ECHA (2014)		
				NOEC	13	ECHA (2014)		
Crustaceans	*Daphnia magna*	Immobility	2	EC10	9660	Richter et al. (2013)		
			21	NOEC	200	ECHA (2014)		
Fish	*Danio rerio*	Mortality	2	EC10	1070	Richter et al. (2013)		

[a] An EC10 for a long-term test which is obtained by extrapolation using appropriate statistics can be considered as a NOEC. This procedure is used if no NOEC is available (EC, 2003a).
[b] The derivation of PNEC is based on the European guideline with an assessment factor of 10 (EC, 2003a).

China, respectively. And it is favorable for us to verify the predicted concentrations in different basins. As only one sample was reported in the Yangtze River for climbazole concentrations, sampling campaigns were carried out by the authors (Pan et al., 2014) and the environmental concentrations were also measured in our laboratory by using our published method (Chen et al., 2012). In brief, two sampling campaigns were carried out in July and December 2013 in the Yangtze River Downstream (ID: 26). Water and sediment samples were collected from 24 sites in clean amber bottles (1 L each, three replicates of each grab sample). Water samples were extracted with solid phase extraction method, while sediment samples were extracted by ultrasonic extraction method. The target chemical climbazole in the extracts of those water and sediment samples was determined with an Agilent 1200 series ultra-high-performance liquid chromatograph (Agilent, USA) coupled to an Agilent 6460 triple quadrupole mass spectrometer with electrospray ionization in positive ionization mode (UHPLC-ESI-MS-MS). The chemical analysis was subject to strict quality assurance and quality control (QA/QC) procedures. Limit of quantification (LOQ) for climbazole was 0.08 ng/L for surface water and 0.11 ng/g dry weight (dw) for sediment. The measured concentrations were expressed as: mean ± standard deviation, as shown in Table S5.

2.4. Risk assessment

A risk quotient (RQ) approach was applied in ecological risk mapping for climbazole in surface water and sediment of each basin based on the predicted environmental concentrations (PECs) and the predicted no-effect concentration (PNEC) according to the European Commission Technical Guidance Document (EC, 2003a). For the risk assessment of sediment, the predicted pore water concentrations (the water subcompartment included in the sediment compartment) were derived and used as the PECs for assessing sediment risks with aquatic toxicity data due to the absence of sediment toxicity data. The PNEC value (0.56 μg/L) for climbazole was derived from the ecotoxicity data in the literature (Richter et al., 2013; ECHA, 2014) (Table 3). The criteria for interpreting the RQ are given as follows: RQ < 0.1, "low risk"; RQ from 0.1 to 1, "medium risk"; and RQ > 1, "high risk" (Hernando et al., 2006). Risk mapping for climbazole in China basins was performed using the software ArcGis 9.3.

3. Results

3.1. Emission estimation of climbazole in the whole China

Based on the consumed amount of hair care products in China in 2011, the annual usage of climbazole in the whole country was estimated to be 345 t (Table 4). If it were uniformly distributed to the whole population (1.3 billion) in China, the *per capita* consumption (PCC) of climbazole would be 257 mg/yr. After treatment in WWTPs, the emission to the receiving environment was estimated to be 254 t. Among the emission to the environment, 23 t of climbazole was discharged into the soil compartment based on the statistical data of wastewater irrigated land, while the rest (231 t) mainly reached to the water compartment.

For each of the 58 basins, the emissions of climbazole into the environment were also calculated and the results are listed in the Supplementary information (SI-A). Due to the tremendous differences in population, large variations existed among the basins. The highest emission for climbazole was 18.9 t, which was found in Huai River basin (ID: 22), and the lowest emission was 0.004 t in Senggecangbu basin (ID: 50). These calculated emission values for water and soil compartments of each basin were then used as the model input parameters for predicting the environmental concentrations and multimedia fate of climbazole.

3.2. Environmental concentrations of climbazole

3.2.1. Predicted environmental concentrations by the fugacity model

The simulated climbazole concentrations for all of the 58 basins were modeled for air, water, soil, sediment, suspended particulate and fish. The results are given in Table S6. It is noted that climbazole was found at much higher concentrations in the water compartment than in the other compartments. For the air compartment, the low Henry's law constant of climbazole (Table 1) resulted in low concentrations, ranging from 8.66×10^{-6} to 1.36×10^{-8} ng/L. Similarly, the climbazole

Table 4
Consumptions of personal care products and climbazole in China for year 2011.

Categories	Consumed amount (t/yr)[a]	Climbazole					
		Content level (%)[b]	Inclusion level (%)[c]	Total amount included in the PCPs (t/yr)	Per person consumption (mg/cap/yr)[d]	Estimated input for the environment (t/yr)	
Shampoo	386,848	4.35	2	345	257	254	Water: 231
Men's hair care	9407						Soil: 23

[a] Consumed amount, the market research sales data, which was obtained from Euromonitor.
[b] Content level, the percentage of consumed products that contained a target chemical, which was obtained from Mintel's New Global New Products Database (GNPD).
[c] Inclusion level, the percentage of the active ingredient in products according to http://ec.europa.eu/health/ph_risk/committees/04_sccp/docs/sccp_o_164.pdf.
[d] Per person consumption = Σ(consumed amount × content level × inclusion level × 10^9)/population. The total population (1,339,724,852 people) was obtained from the report of the Sixth National Census in China.

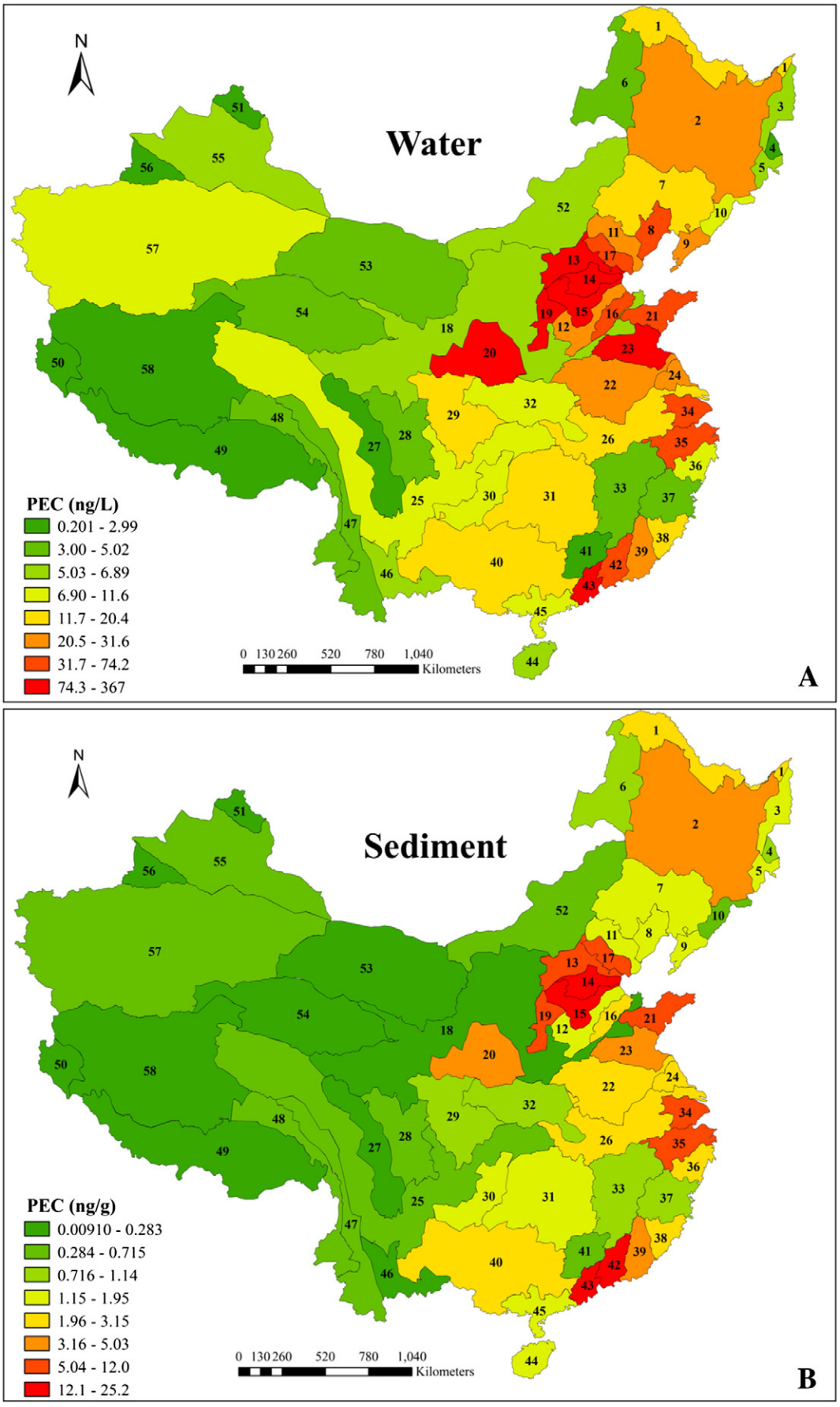

Fig. 2. Exposure mapping for climbazole in water phase (A) and sediment phase (B). The predicted environmental concentrations (PEC) for climbazole are given in water phase with the unit of ng/L, and in sediment phase with the unit of ng/g.

mass into the soil compartment was quite low via diffusion process and wastewater irrigation in some basins (basin IDs: 7–24). The climbazole concentrations in wastewater irrigated soils were found in the range between 2.13×10^{-2} and 7.92×10^{-1} ng/g. The highest concentration in the soil compartment was located in Haihe River basin (ID: 12). As the sub-compartments of water, both suspended particulates and fish showed relatively higher concentrations for climbazole when compared with the soil and sediment compartments. For example, the predicted concentration in fish was as high as 23.3 ng/g in Ziya River basin (ID: 14), which may require a further ecological risk assessment.

The predicted environmental concentrations (PECs) of climbazole in the water and sediment compartments of each basin are shown in Fig. 2. The highest PEC in surface water in China was 367 ng/L, which was found in Ziya River basin (ID: 15), followed by the Daqing River basin (ID: 14; 302 ng/L) and Wei River (ID: 20; 172 ng/L), and all of the basins located in the north China (Fig. 2A). The lowest PECs (0.20–0.51 ng/L) were mainly distributed in Tibet and Xinjiang, including basins of Brahmaputra (ID: 49), Senggecangbu (ID: 50) and Ertix River (ID: 51). In sediment, the simulated climbazole concentrations in sediment ranged from 0.009 ng/g in Senggecangbu basin (ID: 50) of Tibet region with a small population to 25.2 ng/g in Dongjiang River basin (ID: 42) of southern China with a large population (Fig. 2B). As shown in Fig. 2, in both water and sediment compartments, the concentration distribution had a similar trend: east China > west China. The highest climbazole concentrations were all located in Haihe River basin (IDs from 12 to 17), Pearl River basin (IDs from 42 to 43) and Wei River (ID: 20), with very large population densities in the two regions. High PECs were also observed in Huaihe River (basin IDs: 22–23), with populous provinces of Shandong and Henan.

3.2.2. Measured concentrations in Yangtze River

The measured concentrations of climbazole in water and sediment of Yangtze River Downstream are shown in Table S5. In addition to a sample in the sediment, all of the sampling sites were detected with climbazole in both summer (July) and winter (November) seasons. In general, no obvious significant differences were found between the two seasons. The MECs determined in the present study for Yangtze River Downstream were: 0.80 ± 0.42 ng/L (range: 0.14–2.12 ng/L) in surface water and 0.77 ± 0.66 ng/g dw (range: 0.17–4.41 ng/g dw) in sediment (Table S5). These values were used to compare with the predicted environmental concentrations.

3.3. Multimedia fate based on the transfer fluxes

Table 5 lists the average contribution of each transfer flux of climbazole in and out of the air, water, soil and sediment compartments in China. For soil and sediment compartments, degradation flux accounted for more than 95% of the total output flux. It showed that degradation was the main output pathway for these two environmental compartments. In addition to diffusion process and precipitation, the wastewater irrigation contributed one third of the total input flux in the soil compartment. In air compartment, diffusion from water (T_{21d}) contributed most for the input of climbazole and flux of advective flows out of the area through air (T_{10t}) was the main output pathway in air. In water, most of climbazole losses were due to advection output flows. Besides, sedimentation and degradation fluxes also contributed most for the loss of climbazole. The mass inventory of climbazole in China was estimated to be 294 t when a steady state was achieved. In the whole environment studied, 6.79% of the total mass was in water, 83.7% in sediment, 9.49% in soil and 0.002% in air.

3.4. Risks of climbazole in China

Based on the aquatic ecotoxicity data and predicted concentrations, the risks posed by climbazole in water and sediment were assessed for the river basins of the whole China (Fig. 3). No high risks would be expected in water compartment of all river basins (Fig. 3A). But two basins located in Haihe River system (IDs: 14 and 15) were found to be very close to high risk rank, with the RQs of 0.54 and 0.66, respectively. Among all 58 basins, 10 basins were found at medium risks. The medium risks were mainly located in basins of Daling River (ID: 8), Haihe River (IDs: 13–16), Fen River (ID: 19), Wei River (ID: 20), Yishusi River (ID: 23), and Pearl River (IDs: 42–43). The medium risks were mainly located north China. By contrast, the risks posed by climbazole in sediment in river basins of China were much higher than those in water compartment. As showed in Fig. 3B, high risks were found in Tuhai-Majia River (ID: 16) and Dongjiang River (ID: 42). In addition, 17 out of 58 basins were with median risks. The northwest China and southwest China, with the minimum population density in China, were predicted to have minimum risks posed by climbazole no matter in water or in sediment.

Table 5
The contribution of each transfer flux of climbazole in and out of the four compartments. The "in" refers to the input fluxes and the "out" refers to the output fluxes. All the transfer flux symbols are listed in Table 1.

Environmental compartments	Flux percentage			
	In		Out	
Air	T_{21d}	96.1%	T_{12d}	1.09%
	T_{31d}	3.92%	T_{12p}	0.02%
			T_{12w}	0.05%
			T_{13d}	0.16%
			T_{13p}	0.01%
			T_{13w}	0.04%
			T_{10m}	37.1%
			T_{10t}	61.5%
Water	T_{12d}	0.04%	T_{21d}	2.47%
	T_{12p}	0	T_{24d}	0.97%
	T_{12w}	0	T_{24s}	48.7%
	T_{42d}	0.96%	T_{20m}	28.5%
	T_{42r}	0.66%	T_{2f}	1.10%
	T_{32e}	0.04%	T_{20t}	18.2%
	T_{32l}	0.42%		
	T_{02h}	95.7%		
	T_{02t}	2.15%		
Soil	T_{13d}	56.4%	T_{31d}	2.28%
	T_{13p}	3.32%	T_{32e}	0.57%
	T_{13w}	7.60%	T_{32l}	3.35%
	T_{23h}	32.7%	T_{30m}	93.8%
Sediment	T_{24d}	2.10%	T_{42d}	1.83%
	T_{24s}	97.9%	T_{42r}	1.33%
			T_{40m}	96.8%

4. Discussion

Based on the usage of hair care products in China, the exposure concentrations of climbazole in different environmental compartments were predicted using the level III fugacity model. Measured environmental concentration (MEC) data from limited previous studies (Chen et al., 2014; Heeb et al., 2012; Qi et al., 2014) showed general consistency with the simulated concentrations. The MECs reported for Dongjiang River basin (ID: 42) in south China were 87.5 ± 79.2 ng/L (range: 0.753–281 ng/L) in surface water and 25.6 ± 32.5 ng/g (range: 0.257–191 ng/g) in sediment (Chen et al., 2014). These concentration ranges are comparable with the PECs (water: 73.0 ng/L; sediment: 25.2 ng/g) from the fugacity modeling of the present study. The differences between the measured and modeled data in water and sediment in Dongjiang River basin were 0.08 and 0.007 log units, respectively. The reported average concentration in rivers downstream of Beijing was 310 ng/L (Heeb et al., 2012), which is in the same order of magnitude with the PEC (123 ng/L) in Yongding River (ID: 13). Qi et al. (2014) have reported the climbazole concentration at 4 ng/L in Datong station in Yangtze River Downstream (ID: 26), which is 0.68 log unit different to the PEC (19.0 ng/L) for the river. For the Yangtze River Downstream, the differences between our field MECs and PECs (water: 19.0 ng/L; sediment: 3.15 ng/g) were 1.38 and 0.61 log units.

Since the average depth of the Yangtze River Downstream is much larger than the other two rivers Dongjiang and Haihe Rivers (Table S3), the sediment is less affected by other environmental processes. Thus the modeling method was always suitable. But it is not the case for the water compartment. The flux analysis showed that in the Yangtze River Downstream not only the human discharging for climbazole (T_{02h}) but

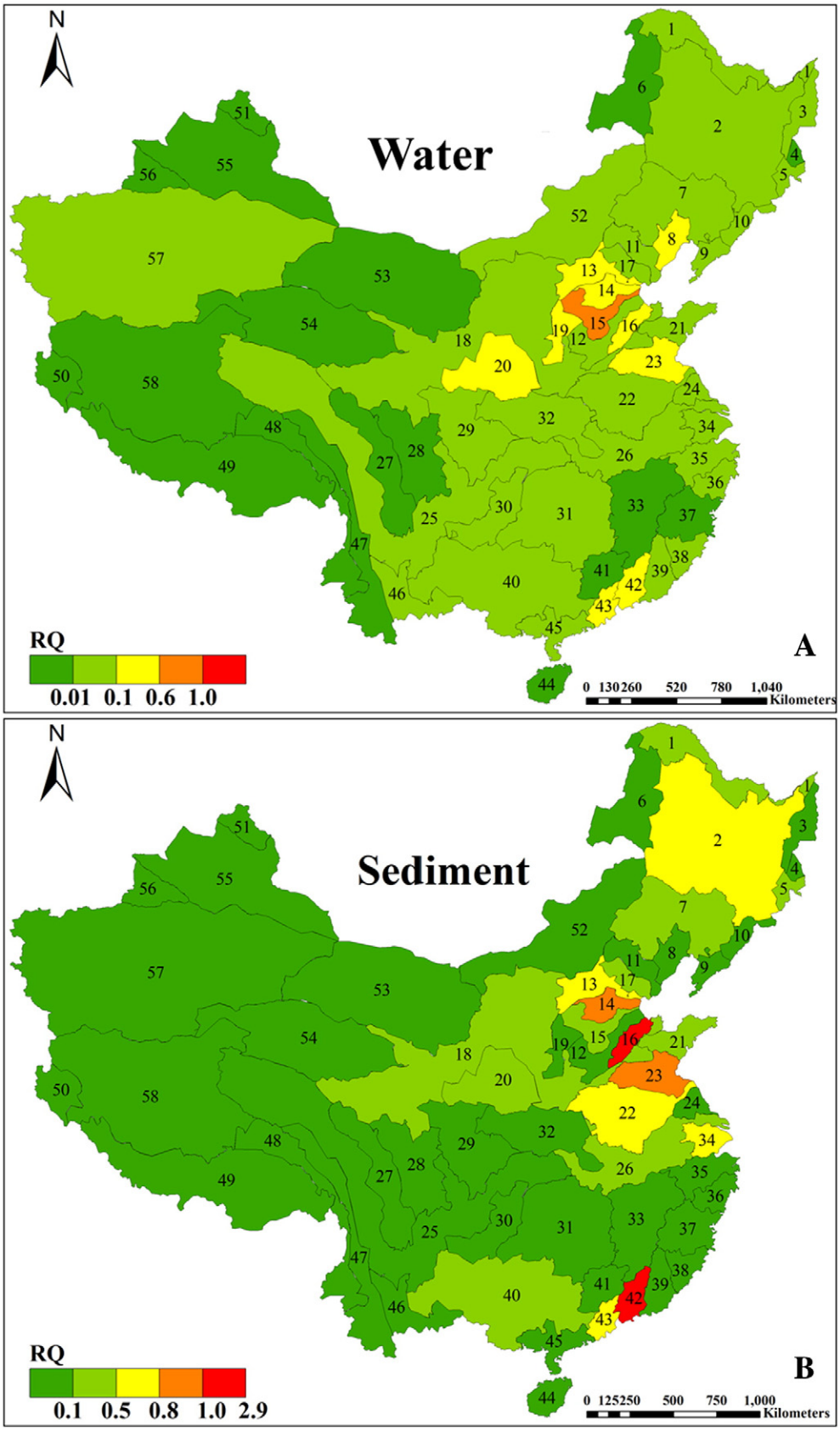

Fig. 3. Risk mapping for climbazole in water (A) and sediment (B). Aquatic risks posed by climbazole are expressed by risk quotients (RQs).

also advective flows in the area through water (T_{02t}) contributed most for the input of the target chemical. The Yangtze River Downstream received the output water flows from four big basins (Dongting Lake, Hanjiang River, Poyang Lake, Taihu Lake), as well as the upstream of Yangtze River (SI-B). However, due to the influence of Three Gorges Dam and large-scale sand mining, the advective fluxes from these rivers into Yangtze River are limited (Xu et al., 2013). If we exclude the role of advective input flows from these five basins to Yangtze River Downstream, the amount of the target chemical into the Yangtze River Downstream would be reduced accordingly. Under this assumption, the predicted concentrations in the water compartment would be closer to the MECs (the difference was around an order of magnitude). As the longest and largest river in China, the uncertainties of modeling for Yangtze River might be very large. The Yangtze River needs to be sectioned into more sub-basins in order to have better simulation due to its complex environmental conditions. In general, the concentration levels in the whole China for climbazole were successfully mapped in the present study. And those measured concentrations for climbazole from the previous studies were from three parts of China: north China (Haihe River), central China (Yangtze River Downstream) and south China (Dongjiang River), and they are generally consistent with the PECs predicted by the fugacity model (Fig. 2A).

The sensitivity analysis showed that advection flow was also the most influencing parameter for predicting concentrations of climbazole in water, so the mainstream of each basin may receive a large amount of climbazole, resulting in high concentrations in delta regions such as the Pearl River Delta. The sedimentation process resulted in further accumulation of climbazole in sediment. For the soil compartment, the wastewater irrigation contributed one third of the total input flux, and the predicted soil concentrations in the irrigated soils may be underestimated as they were averaged for the soil compartment of the whole basins. For the basins with wastewater irrigation (IDs from 7 to 22), the mass contribution from wastewater irrigation was more than 99%. Heeb et al. (2012) reported that more than 95% of the climbazole loading in the downstream of Beijing (located in Yongding River basin, ID: 13) was diverted to the irrigated agricultural soil, since over 90% of the discharge in Beijing was used for irrigation in agricultural land in their study. However, in the present study, the mass portions in Yongding River basin were 0%, 9.07%, 32.6%, and 58.3% for air, water, soil and sediment, respectively. Overall, after release of climbazole to the water and soil compartments, followed with various environmental processes, it would be accumulated in various environmental media with different proportions. Slow dissipation for climbazole has been reported in field soils, with its half-lives more than 150 days (Chen et al., 2013). Therefore, climbazole would persist in the soil and sediment compartments.

Of all the modeling parameters, rate of the chemical entering into water by human (T_{02h}) and area of water phase (A_2) were the most sensitive parameters in the prediction of water phase concentrations (Fig. S1). The uncertainties were displayed in terms of SQR, which are presented as the shaded area (see Fig. S1). Most SQR calculated for climbazole concentrations in water varied within one order of magnitude, with the largest of 0.9 log unit for Heilongjiang basin (ID: 1) and the smallest of 0.5 log unit for Hainan basin (ID: 44). Although uncertainties about emission for climbazole in the 58 basins have been taken into consideration by using Monte Carlo analysis, more uncertainty still existed. As the consumption for PCPs is related to the GDP per capita (Hodges et al., 2012), the uncertainty from emission of climbazole would be reduced if the usage inventory for each basin was available. But in the near future, the statistic data for PCPs in each basin in China will not be available because the chemical registration system has not been established at the county level in China. Based on the results of uncertainty analysis and comparison between the PECs and MECs, the model presented here was still considered to provide a good simulation for the fate of climbazole in the environment.

Given a great proportion of emitted climbazole ending up in sediments (the mass inventory in sediment accounting 83.7% of total mass), the risks in sediment in river basins of China were relatively high. Among all the basins, the Haihe River (IDs: 11–17) and Pearl River (IDs: 40–43) were with higher risks posed by the climbazole. And medium risks were mostly concentrated in north China. Although no high risks would be expected in water compartment of Chinese basins, previous monitoring studies showed co-occurrence of azole fungicides with climbazole in surface water (Kahle et al., 2008; Chen et al., 2012, 2014; Huang et al., 2010; Peng et al., 2012; Wick et al., 2010). These chemicals could impose similar ecotoxicological effects to the aquatic organisms (EC, 2003b; van Wijngaarden et al., 1998; Richter et al., 2013), thus resulting in additive effects (Coors and Frische, 2011). Hence, higher aquatic risks are expected from this group of chemicals in household and personal care products. Further investigations are required in order to assess the realistic risks to aquatic organisms in Chinese aquatic environments.

5. Conclusion

It is the first report on the emission and multimedia fate of climbazole in the whole China based on the usage data of related personal care products (PCPs). The usage of climbazole as ingredient in PCPs was estimated to be 345 t, and the total emission to the environment was 245 t, with approximately 93% discharged into the water compartment and 7% into the soil compartment. A level III fugacity model was successfully applied to estimate the contamination levels and fluxes of climbazole across various environmental compartments at the basin scale in the whole China. Based on the preliminary risk assessment, 2 out of 58 basins in China were with high risks in the sediment. The medium risks in water and sediment were mostly concentrated in north China. More realistic risk assessment would be possible only when more chronic ecotoxicity and fate data for climbazole and co-existing PCPs are available.

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Appendix A. Supplementary data

Detailed description of the calculation method and parameters, tables of data, and additional figures are available in supplementary information. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.scitotenv.2015.03.038.

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