Potential Impacts of Future Climate Change and Emission on the Fate and Transport of PFOS in the Bohai Rim, China

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Abstract:

Both climate change and contaminant emission rate are expected to affect the transport and fate of POPs. However, studies on their integrative impacts are fewer. This study, taking Perfluorooctane Sulfonate (PFOS) as an example, explored how future climate change and contaminant emission affect the fate of POPs synthetically, as well as urbanization rate being taken into account, using BETR-Urban-Rural (BETR-UR) model, an improved BETR model. The results suggested that climate change had significant effects on the fate of PFOS, with precipitation and temperature

being predominant factors, by the following aspects: advection processes, degradation rate, and intermedia transfer processes. Under the "business-as-usual" emission scenario, for most grids, a remarkable decline in PFOS concentration was observed in fresh water and urban soil in the future, particularly in the late 21st century, while coastal water and rural soil displayed an opposite changing trend. Besides, under the integrative effects of reducing emission and climate change scenarios, PFOS concentrations in each compartment decreased sharply over time. Additionally, we discussed the influences of climate change on the fluxes of PFOS to the Bohai Sea. Total sum of emissions increased by 1.61%, 11.80%, 17.04% with increasing precipitation, and sinks by 2.59%, 14.30%, 22.24% due to volatilization and degradation flux in 2035, 2065, and 2100, respectively. However, the sum of the emissions was always more than the sum of the sinks in Bohai Sea. The coastal or marine ecosystem should be given greater consideration in the future. This suggests that future assessment of climate change impacts on POPs fate should take emission reduction into consideration.

Keywords: climate change, emission rate, urbanization, PFOS fate, multimedia model, regional scale

1. Introduction

Persistent organic pollutants (POPs) are a kind of pollutants with the following properties: persistence, toxicity, and long-range atmospheric transport (LRAT). Due to these properties, particularly the LRAT resulting in dispersed contamination far from source regions, the fate and behavior of POPs have captivated increasing concern from international environmental organizations, governments, academics, and the public. Many researches showed that the fate and behavior of POPs have been affected by various factors, e.g. emission rate, environmental parameters such as temperature, rain rate, and soil solids organic carbon fraction. (Prevedouros et al., 2004a; Prevedouros et al., 2004b). Climate change is having far-reaching effects on the environment and then on the fate of POPs, not only impacted by and impacting on natural processes within the climate system itself, but also anthropogenic activities (e.g., increased emissions of greenhouse gases) (Paul et al., 2012). Direct changes such as temperature rise, and those driven by it (ocean temperature rise, sea-level rise), altered precipitation patterns, wind and

ocean current patterns, hence resulted in those indirect changes such as land cover changes.

In general, the influencing mechanism of climate change on the environmental behavior and fate of POPs could be described from three aspects. Firstly, it is likely to influence the environmental behavior of POPs by enhancing the volatilization from primary and secondary sources, by influencing their partitioning between soil, sediment, water, and atmosphere, including air-surface exchange, wet/dry deposition, and reaction rates (Teran et al., 2012). Secondly, it could change the solubility of chemicals, and consequently change their concentration and activity in the environment. Then, it could affect the decomposition rate of POPs in the environment (Zhou and Ma, 2013). However, our understanding of these mechanism is mostly qualitative, and a more quantitative description of potential effects is needed (Woehrnschimmel et al., 2013). Recently, a few studies have explored the effects using models under climate change scenarios quantitatively (Gouin et al., 2013; Lamon et al., 2009; Ma and Cao, 2010; Paul et al., 2012). Lamon et al. studied fate and transport of PCBs under a realistic climate change scenario using global multimedia model under steady state (Lamon et al., 2009). On regional scale, Paul et al. and Henry et al. explored the potential implications of future climate and land-cover changes for the fate and distribution of POPs in Europe and Arctic, respectively (Paul et al., 2012; Woehrnschimmel et al., 2013). The common modeled results showed that the effect of climate change on environmental concentrations of POPs was typically up to factors between 1.5 and 2.5 even up to 4 in modeled concentrations. While, PCB 153 displayed a change with the most reduction in burden of up to 40% in some Mediterranean compartments in Europe (Paul et al., 2012). However, the researches combining climate change and emission rate to study the integrated effects are fewer.

The objective of this study is to explore how climate change (temperature, precipitation, wind speed, soil carbon stock, and sea-level rise) and emission rate affect the fate of perfluorooctane sulfonate (PFOS), as well as the urban-rural disparities, with a facus on Bohai Rim in China. In this study, the Berkeley-Trent-Urban-Rural (BETR-UR) model was used to run the simulations under the three climate change scenarios (B1, A1B, and A2) in IPCC 2007 and four emission scenarios for three 20-year periods throughout the 21st century (2016-2035, 2046-2065, and 2081-2100), relative to the baseline simulation of 2010. Then, it explored the key affecting factors of PFOS, and analyzed the alterations of mass fluxes of PFOS to the Bohai Sea under climate change. This research could provide powerful theoretical support for PFOS emission reduction

and ecosystem protection.

2. Methods and Materials

2.1 Model description and study area

Within the original BETR model based on fugacity concept (Mackay, 2001), a connected system of nine discrete and homogeneous compartments is considered as one segmentation (or grid). BETR model has been successfully applied to model the multimedia fate of chemicals, including the North America (MacLeod et al., 2001; Woodfine et al., 2001), Europe (Prevedouros et al., 2004a; Prevedouros et al., 2004b), and the global environment (MacLeod et al., 2005). The BETR-UR model is an improved BETR model (Song et al, 2016). It takes the effects of urbanization into account, dividing the soil and lower air compartments into urban soil and rural soil, lower urban air and lower rural air, respectively. The urban areas mainly indicated those areas with high population density, including industrial land, built-up land, commercial districts, urban residential areas, municipal land for public facilities, and their buffers. Except for urban areas, we defined rural areas as a combination of rural villages, agricultural land, grassland, forest land, rural residential areas, unused land and so on (Wang et al., 2010). The framework of BETR-UR model is illustrated in Fig. 1. In the BETR-UR model, the environment within each segment contains nine compartments. Specific environmental parameters for an urban area like urban perimeter, urban-rural atmospheric mixing rate, freshwater area of urban area etc. and transfer processes between urban and rural area were also improved. More materials could be found in (Song et al., 2016).

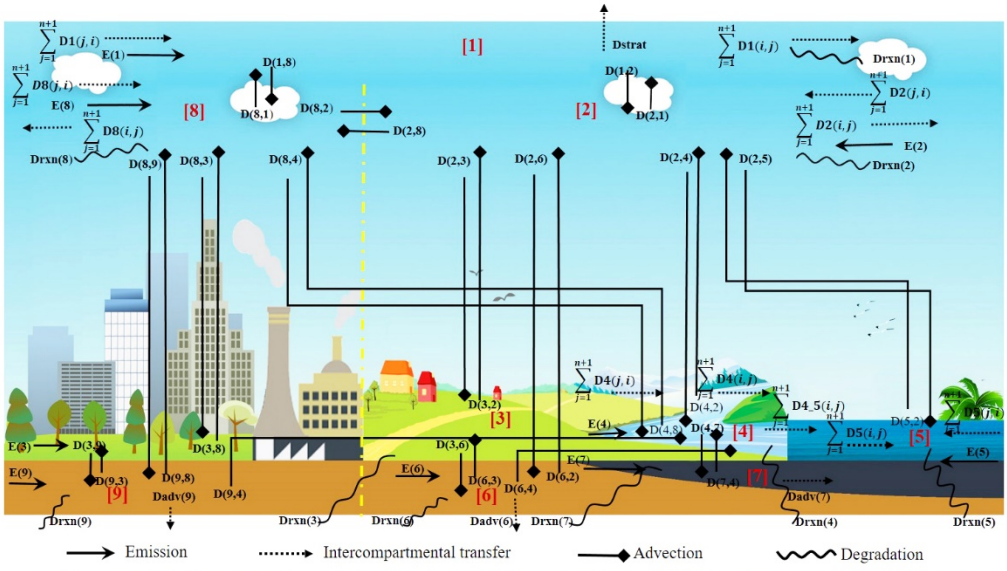

Fig. 1 Contaminant transportation processes in the region *i* linked with *j* in the BETR-UR model.

The Bohai Rim, including part of Bohai Sea and its surrounding area, is one of the most prosperous regions in China. In this paper, the study area included Beijing, Tianjin, Liaoning, Hebei and Shandong provinces and municipalities. A wide range of industries are distributed in this region, including textile treatment, metal plating, production of firefighting chemicals and semiconductor industries, some of which are associated with industrial sources of PFOS and related substances in China (Xie et al., 2013b). Rapid urbanization and industrial development have caused great increase in energy consumption and pollutants emission, further leading to multiple environmental problems.

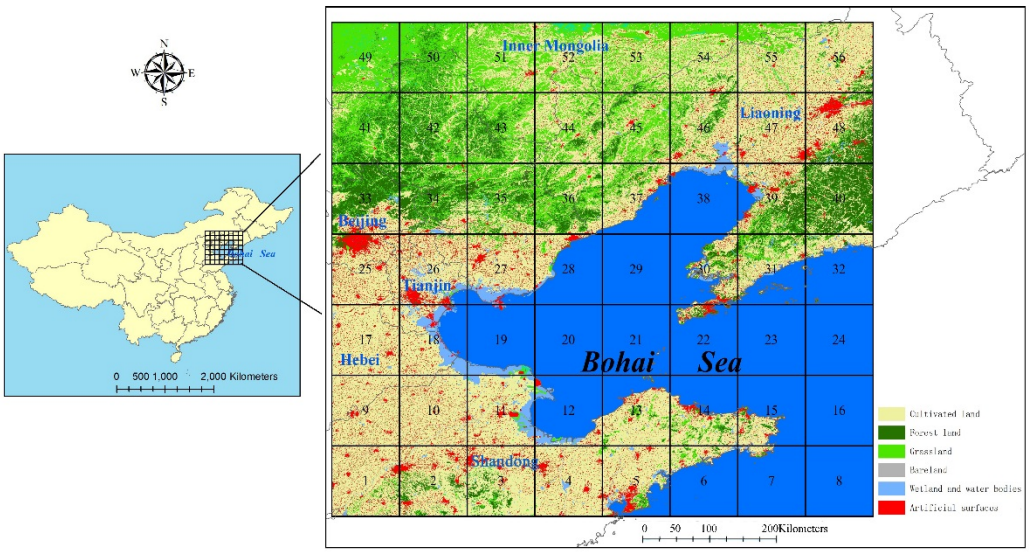

Fig. 2 Study area and model segmentation.

The longitude of Bohai Rim is from 116°E to 124°E, and the latitude is from 36°N to 43°N. It is divided into 56 grids by 1°×1° (Fig. 2). For the study area, each grid contained 8 compartments which are lower rural air, lower urban air, rural soil, urban soil, fresh water, fresh water sediment, coastal water, and vegetation. The effects of upper air were ignored as the influence of long-range air transport within this region was considered to be limited. The 56 sub-grids are linked by advection of air, fresh water and coastal water between adjacent segments, and the runoff of fresh water to coastal water was also considered.

2.2 Physico-chemical properties of PFOS

PFOS, as one of the most abundant old-generation members of PFAS family, is a kind of emerging POPs, and is one of the pollutants that are most difficult to degrade. PFOS and related substances are synthesized chemicals manufactured for their desirable properties of chemical stability, high surface activity, and water and oil repellence (Giesy and Kannan, 2001, 2002). China began to produce PFOS-based products at a large scale in 2004, and the annual production of PFOS-related chemicals grew rapidly from 2003 to 2011 (Xie et al., 2013a). The physical-chemical properties of PFOS included in the BETR model are listed in Table 1 (Liu, 2014). Additionally, in view of both hydrophobic and hydrophilic properties of PFOS (Brooke et al., 2004), improvements were made to the calculation of PFOS partition coefficient duo to the influence of water salinity on the sorption behavior. Full details are available in the study by (Liu et al., 2015).

Table 1 Physico- chemical properties of PFOS

Properties	MW	M.P.	Solub	V.P.	Log(K_{OW})	Log(K_{OA})	$\tau_{1/2}$ LA
PFOS	538.54	400.00	519.00	3.31E-04	4.88	11.73	265500
Properties	$\tau_{1/2}$ Soil	$\tau_{1/2}$ Veg.	$\tau_{1/2}$ FW.	$\tau_{1/2}$ CW.	$\tau_{1/2}$ Sed.	E.P.	E.S.
PFOS	100000000	265500	5500000	5500000	17000000	50000	-20000

Notes: molar mass (MW, g/mol), melting point (M.P., □), aqueous solubility (Solub, g/m^3), vapor pressure (V.P., Pa), lower air reaction half-life ($\tau_{1/2}$ LA, h), soil reaction half-life ($\tau_{1/2}$ Soil, h), vegetation reaction half-life ($\tau_{1/2}$ Veg., h), fresh water reaction half-life ($\tau_{1/2}$ FW., h), coastal water

reaction half-life ($\tau_{1/2}$ CW., h), sediment reaction half-life ($\tau_{1/2}$ Sed., h), enthalpy of vaporization from water to air (E.P., J/mol) and enthalpy of solution from octanol to water (E.S., J/mol).

2.3 Emission scenarios

According to the methodology and emission inventory developed by our research group (Xie et al., 2013a; Xie et al., 2013b), spatially distributed emissions of PFOS and its related substances were estimated for the study area in 2010, which was under the hypothesis that all PFOS related substances immediately degraded to PFOS (Liu et al., 2015). In this study, four different future emission scenarios were proposed for the three 20-year periods to the year 2100. The emission scenario 1 is called "business-as-usual (BAU)" scenario, under the assumption that annual PFOS emission continues in the future till 2100. Since PFOS and its related substances were listed in Stockholm Convention on POPs in 2009, the production of PFOS-related chemicals fluctuated and stabilized at around 250 t/a in China from 2009 (Xie et al., 2013b). So the PFOS emission till 2100 was assumed to be the same as in 2010. This is also a reference scenario in order to explore the effects of climate change. Under this assumption, the emissions to each compartment including fresh water, urban soil, rural soil, urban air, and rural air kept constant. The reason for this assumption is that, it is easier to manage and implement the pollution control measures in urban areas even if the population and land-use area of urban areas would increase till 2100. For rural areas, even though the population and land-use area would decrease by time (more details are referred to Section 2.4), along with the shift of industrial development from urban to rural areas and the improvement of people's living standard, the industrial and domestic emissions would almost continue.

The emission scenarios 2, 3, and 4 are on the hypothesis that China would begin to phase out PFOS and similar chemicals, and use alternatives fully by 2030, 2050, and 2100, respectively, in compliance with the international treaties and national regulations. It is assumed that the PFOS emission would linearly decrease to zero from 2016 until the year of withdrawal. Since the Chinese government set a series of regulations on the production and use of PFOS in 2014 to abide to the Stockholm Convention, thus encouraging the development of alternatives, while it did not determine the withdrawal year, we set the above three scenarios in this study. After the

withdrawal year, releases will not be suddenly stopped because of applications by secondary users. For all secondary users (metal plating, firefighting, textile, semiconductor, and domestic users), a worst-case situation is given in which the storage of each one was within its shelf life and all expired products would be treated on time. Hence, emissions from storage of secondary products would continue being released during shelf-life period. Remarkably, there are some differences between industrial sectors and domestic users in the future emission. For industrial sectors, taking fire-fighting sector as an example, the shelf life of products is 5 years, then the releases would be as the same as the previous for 5 years. For domestic applications, releases would be assumed to reduce linearly as products come to the end of their natural life. For example, carpets are in use for an average of about 10 years, releasing one tenth of their treatment each year until eventual disposal (Paul et al., 2008). In addition, PFOS-polymers released from textile processes would degrade after 30 years, because the half-life of PFOS-polymers is longer and even more than 30 years, and the transforming factor was 0.3 (Brooke et al., 2004). Finally, the future simulations of the three 20-year periods were under the annual mean emission of each period. The estimated total emissions of PFOS and their compartment distributions for the four scenarios are listed in Table S1.

2.4 Brief introduction to climate change and urbanization scenarios

The following changes were implemented for each climate change scenario (Special Report on Emission Scenarios (SRES) B1, A1B, and A2 in IPCC 2007): precipitation, temperature, sea-level rise, soil carbon stock, and wind speed. The SRES scenarios explore alternative development pathways, covering a wide range of demographic, economic and technological driving forces and resulting greenhouse gas emissions. B1 describes a convergent world, a global population that peaks in mid-century, but with more rapid changes in economic structures toward a service and information economy. The A1B assumes a world of very rapid economic growth, a global population that peaks in mid-century and rapid introduction of new and more efficient technologies but a balance across all sources. A2 describes a very heterogeneous world with high population growth, slow economic development and slow technological changes. The global average best estimate temperature changes at 2090-2099 relative to 1980-1999 were 1.8□, 2.8□,

198 3.4□ for those three scenarios, respectively. More introductions about SRES B1, A1B, and A2
199 could be found in IPCC Climate Change 2007 Synthesis Report (IPCC, 2007). In this paper, the
200 climate change scenarios were referred to some literatures focused on China of which the results
201 were based on IPCC 2007. More details are as follows.

202 - Precipitation

203 Gridded 10-year averaged precipitation rates in the study area were extracted from (Zhang et
204 al., 2012) for the periods 2016-2035, 2046-2065, and 2081-2100 (short of 2035, 2065, 2100 the
205 following, also called early, mid, and late 21st century respectively). Precipitation was projected to
206 increase over the study area by 3%-9% (10 yr)$^{-1}$, 7.5%-18% (10 yr)$^{-1}$, and 9%-18% (10 yr)$^{-1}$
207 respectively, under all three scenarios for the three periods.

208 - Temperature

209 The same process was repeated for surface air temperature (Zhang et al., 2012). The warming
210 rate was projected to increase over the study area by 0.2-0.6□ (10 yr)-1, 0.3-0.6□ (10 yr)-1, and
211 0.1-0.6□ (10 yr)$^{-1}$ respectively, under all three scenarios for the three periods. Additionally, the
212 significant feature of urbanization is "urban heat island effect", and the temperature difference
213 between urban and rural area was 2-6□ (Martine and Marshall, 2007). Hence, this effect was
214 taken into account in the BETR-UR model, and it was assumed to be 4□ for that difference.

215 - Sea-level rise

216 The mean rate of averaged sea-level rise in China was 3.0 mm yr^{-1} between 1980 and 2014. It
217 was inferred that the sea-level of Bohai Sea in the early 21st century was 0.045 m higher than that
218 in 2010 for all three scenarios (China Sea Level communique 2014). The sea-level rise in mid and
219 late 21st century was referred to the global mean data in IPCC AR5, being 0.26 m, 0.25 m, 0.30 m
220 and 0.47 m, 0.48 m, 0.63 m higher under three scenarios, respectively (IPCC, 2014).

221 - Soil carbon stock

222 The simulated averaged soil carbon stock increased by 5% for 2030s, and by 3% for 2090s
223 under scenarios B1 and A2 for northeastern China (Peng et al., 2009). Hence, it is assumed that it
224 increased by 4% for the 2060's under those two scenarios. Furthermore, since scenario A1B is a
225 moderate one between B1 and A2, we supposed that projected averaged soil C stock had the same
226 growth with those two scenarios. Additionally, a study showed that soil carbon stock was about
227 57.76% lower in urban land than that in non-construction land (forest land and green open spaces)

228 (Tao et al., 2015), which was taken into consideration in the model.

229 - Wind speed change

230 A study using all climate model predicted that the annual mean wind speeds in China for the
231 21st century varied slightly under all three scenarios (Jiang et al., 2010). It was projected that mean
232 wind speed increased 0-1 m/s under the three scenarios for the early, mid and late 21st century in
233 the northern part of Northeastern China, middle reaches of the Yellow River and southwest of
234 Tibetan Autonomous Region. Moreover, it increased a little more under scenario A2 than the other
235 two scenarios, and it also increased more in the mid and late 21st century than the early 21st
236 century (Jiang et al., 2010). In this paper, we considered that it had a similar change pattern in the
237 Bohai Rim and northern part of Northeastern China, middle reaches of the Yellow River.

238 Besides, rainfall-runoff relationship and urbanization rate projections were analyzed. The
239 former was referred to the regression model relating mean annual runoff to mean annual
240 precipitation and mean annual temperature by (Chen and Wang, 2004). Rapid urbanization is one
241 of the outstanding features in China, particularly in coastal regions, and China is now at the peak
242 of its urban transition, where rural-urban migration has been a much more important contributor to
243 the growth (Martine and Marshall, 2007). Urban form and function also help define the nature of
244 the interactions between cities and local climate change. For example, the "urban heat island effect"
245 resulting from the impacts of different land uses in urban areas, creates microclimates and health
246 consequences. The size of the urban center, the type of urbanization, urban form, function and
247 land use all contribute to the effect. As villages grow into towns and then into cities, their average
248 temperature increases from 2 to 6 °C above that of the surrounding rural areas (Martine and
249 Marshall, 2007). Since the percentile urbanization trend of Asia from 2000 to 2050 was almost
250 consistent with the curve of urban percentage of Europe from 1950 to 2000, we therefore, assumed
251 that the rate of urbanization of China from 2051 to 2100 was likely the same as that of Europe
252 from 2000 to 2050 (Das Gupta et al., 2014).

253 ## 3. Results and discussion

254 ### 3.1 Model output and validation

255 The simulations were run 18 times on steady state solutions, under each climate change

scenario for each emission scenario. The previous research showed that soil, coastal water, fresh water, and sediment were the top four sinks for PFOS, and the storage in air and vegetation was less than 1.00 %. Consequently, the concentrations and transfer process in urban soil, rural soil, coastal water, fresh water, and sediment were mainly analyzed in the results of this study. The median values of modeled PFOS concentrations in 2010 in fresh water, sediment, urban soil, and rural soil were 8.27 ng/L, 0.38 ng/g, 0.26 ng/g, and 0.11 ng/g, respectively. Additionally, model accuracy was assessed by comparing simulated baseline PFOS concentrations with measured data in fresh water, fresh water sediment, urban soil, and rural soil in the study area (Table S1). Available measured data for PFOS concentrations around the year 2010 were collected from published sources, mostly by our research group (Li et al., 2011; Meng et al., 2015; Wang et al., 2014; Wang et al., 2015; Yang et al., 2011; Zhao et al., 2014; Zhao et al., 2013; Zhu et al., 2014). The results showed that the range of simulated concentrations were generally well consistent with the measured data for all the compartments.

3.2 Spatially projected concentration changes of PFOS

3.2.1 Projected concentration changes of PFOS under emission scenario 1

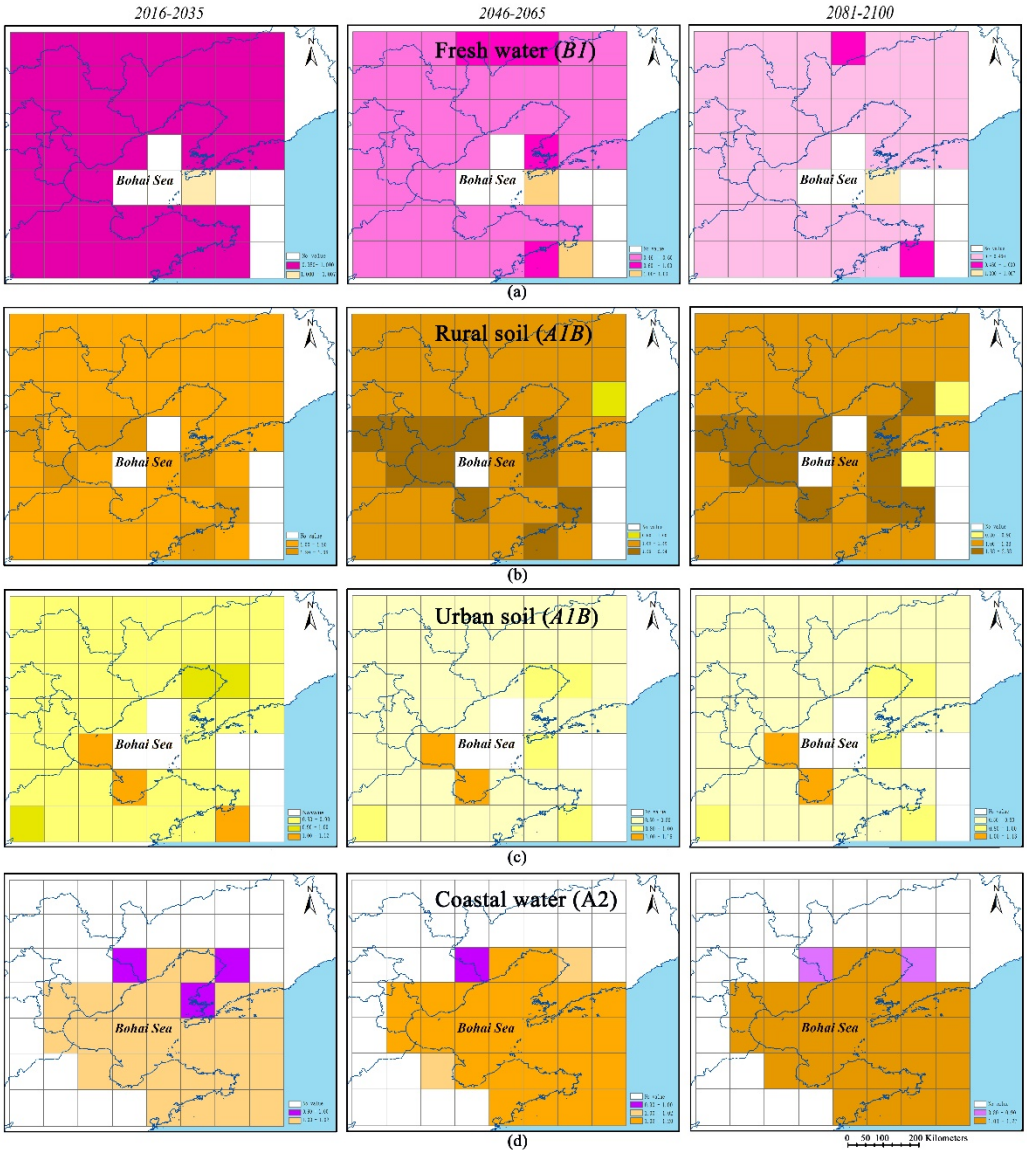

Fig. 3 Projected changes of PFOS concentrations in fresh water, rural soil, urban soil and coastal water under specific climate change scenario for emission scenario 1.

Ratio of projected period concentration and baseline concentration was used to describe the change of PFOS concentration in this study.

Concentration changes of PFOS for fresh water, coastal water, urban soil, and rural soil under three future climate change scenarios and four emission scenarios were listed in Table S3. It showed that there were similar changing trend for those four compartments among three climate change scenarios B1, A1B and A2 under each specific emission scenario. Fig. 3 showed the projected changes of PFOS concentrations in those four compartments under specific climate change scenario for emission scenario 1. It could be seen that a remarkable decrease in PFOS

concentration in the future simulations was observed in fresh water and urban soil (except for some grids). Taking grid 26 (Haihe River in Tianjin City) as an example, the concentration ratios in the early, mid, and late 21st century for fresh water were 0.9616, 0.5394, 0.2772, and for urban soil were 0.8708, 0.7530, 0.7533 under climate change scenario B1. And under scenarios A1B and A2, fresh water concentration ratios were 0.9414, 0.4849, 0.2529 and 0.9750, 0.5203, 0.3179 in the future three periods, the urban soil concentration ratios were 0.8698, 0.7515, 0.7546 and 0.8693, 0.7504, 0.7537 in the future three periods, respectively. Fresh water was observed with the most rapid decline. The key reason for that was the increased runoff with increasing precipitation even though it brought the PFOS in air to aquatic and terrestrial ecosystems through wet deposition and rain dissolution with the increasing precipitation. According to the regression relationship between runoff and precipitation, temperature (Chen and Wang, 2004), the runoff increased a lot, particularly for the mid, and late 21st century, with a value by 5%, 25%, 32% in the future three periods, respectively, under scenario B1. On the other hand, warming water would reduce the solubility of PFOS (Zhou and Ma, 2013). For the urban soil, it might be because the industrial and domestic emissions kept constant under the assumption of industrial shift from urban to rural areas and managed domestic consumptions while with the higher urbanization rate and extended urban land. On the other hand, concentrations of PFOS would decline driven by temperature increasing volatilization and microbial decomposition rate. And this volatilization effect driven by temperature was more significant in urban areas than rural areas because of the urban heat island effect.

On the contrary, for most grids, the concentrations of PFOS in rural soil and coastal water had the opposite trends. Taking grid 26 (Tianjin City) as an example, for rural soil, the concentration ratios were 1.1705, 1.3855, 1.4618 in the future three periods under scenario A1B, and the ratios for coastal water were 1.0029, 1.1688, 1.2259 under scenario A2 in the future three periods, respectively. For coastal water, the runoffs from fresh water to coastal water increased greatly owing to the higher temperature and precipitation, with a value of 14%, 32%, and 38% in the future three periods, respectively. This would bring out the accumulation of PFOS in coastal water. It was consistent with that coastal water was the final sink for PFOS (Liu et al., 2015). For rural soil, under the BAU emission assumption that the related domestic consumptions increased and industries clustered in rural areas while the population and land-use areas decreased in section

2.3, it was reasonable to show a higher concentration in the future.

3.2.2 Projected concentration changes of PFOS under emission reduction scenarios

Fig. S1- S3 showed the projected changes of PFOS concentrations in fresh water, rural soil, urban soil and coastal water under specific climate change scenario for emission scenarios 2, 3 and 4. For emission scenario 2, the PFOS concentrations in fresh water in the whole area will decreas 65% or above in the early 21st century. However, in the mid 21st century, there will be some growth in the southern Bohai Rim comparing to the early 21st century, and for a small number of grids, the PFOS concentrations are higher than 2010. This was closely related to the emission of PFOS. Because in the mid 21st century, the PFOS emission will only be from textile sector, and which in the grids of southern Bohai Rim is higher than the early 21st century under the assumption of emission scenario 2. For rural soil and urban soil, the PFOS concentrations will decrease in the early 21st century, and decrease more in the mid 21st century except for a tiny number of grids. And coastal water is the final sink of PFOS, for a big number of grids, the concentrations are higher than the early 21st century, even for 2010. The trends of other three compartments are almost consistent with the fresh water, because fresh water is the only medium of PFOS released into the environment in the mid 21st century (Fig. S1 and Table S3).

For emission scenarios 3 and 4, the PFOS concentrations in the four compartments will reduce with the linear emission reduction over time except for a few grids. Particularly for emission scenario 3, with the PFOS withdrawn in 2050, the PFOS concentrations will decrease a lot in the late 21st century, by 10 to 10,000-fold (Fig. S2, S3 and Table S3).

3.3 Annual mass flux changes of PFOS in Bohai Sea

In order to explore the impacts of climate change on the fluxes of PFOS to the Bohai Sea, total annual mass flux changes were discussed under emission scenario 1 and climate change scenario A1B because it was a moderate choice.

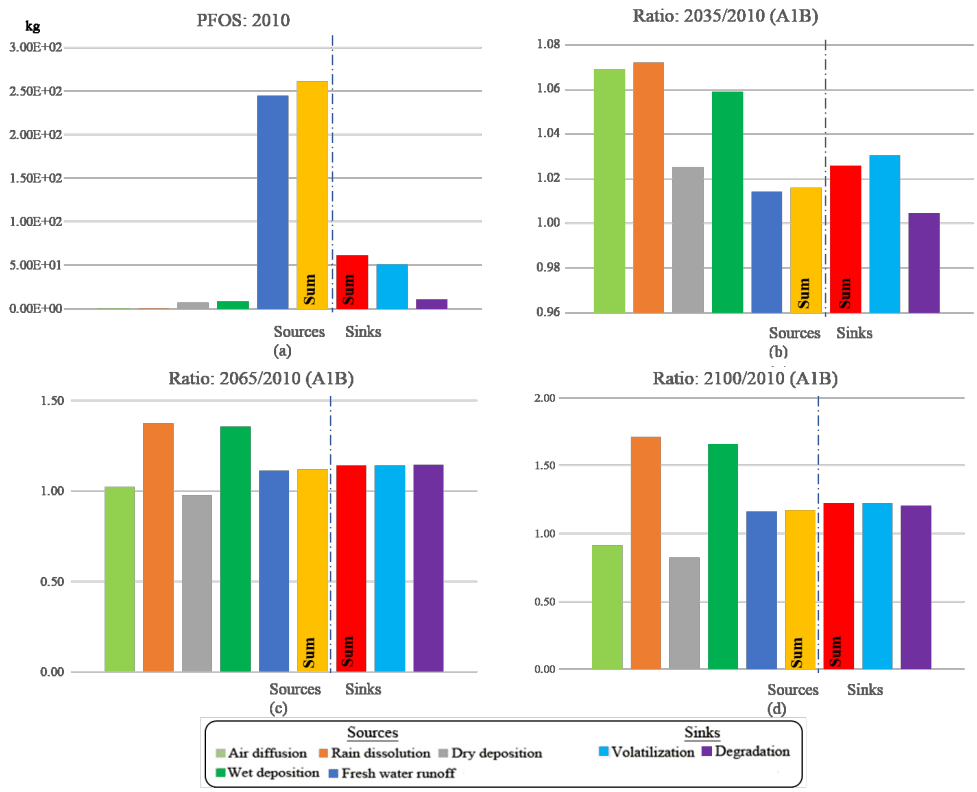

Fig. 4 Total annual mass fluxes (kg), to the Bohai Sea, sources and sinks for (a) 2010. Ratios of total annual mass fluxes: (b) 2035/2010, (c) 2065/2010, and (d) 2100/2010 under scenario A1B.

Total annual mass fluxes of PFOS to the Bohai Sea for baseline 2010, and the ratios of the fluxes for the years 2035/2010, 2065/2010 and 2100/2010 were presented in Fig. 4.

For pathways of PFOS to the Bohai Sea, rain dissolution, wet deposition, and fresh water runoff all will increase somehow in the three future periods, relative to the baseline 2010. Rain dissolution will be up by 7.21%, 37.39%, 71.00%, wet deposition will increase in ascending order by 5.91%, 35.62%, 65.94%, while fresh water runoff will increase by 1.42%, 11.39, 16.30% in 2035, 2065, and 2100, respectively, relative to 2010. These changes are due to increased precipitation in the future. Air diffusion and dry gas deposition firstly increase a little in 2035, then decrease more in 2065 and 2100, remains lower than volatilization and degradation. For sink pathways, volatilization and degradation fluxes both will increase more in the future, relative to the present (2010). This is because of the increased air and water temperature and wind speed. Total sum of sources will increase by 1.61%, 11.80%, 17.04%, and that of sinks by 2.59%, 14.30%, 22.24% in 2035, 2065, and 2100, respectively. However, the sum of sinks in 2010 was

much lower than the sum of sources to the Bohai Sea, so the sum of the sources (left side of the dotted line) is always more than the sum of the sinks (right side of the dotted line), and the differences between the sum of the sources and the sum of the sinks will be larger in the future. This added to the evidence that PFOS concentrations in coastal water would increase more in the future periods. It was inconsistent with the modeled results of γ-HCH and PCB 153 in the North Sea (O'Driscoll et al., 2014). So the general result was that there were big influences of climate change on the mass fluxes of PFOS to the Bohai Sea.

3.4 The changes of PFOS fate and transportation: taking Tianjin city as a case

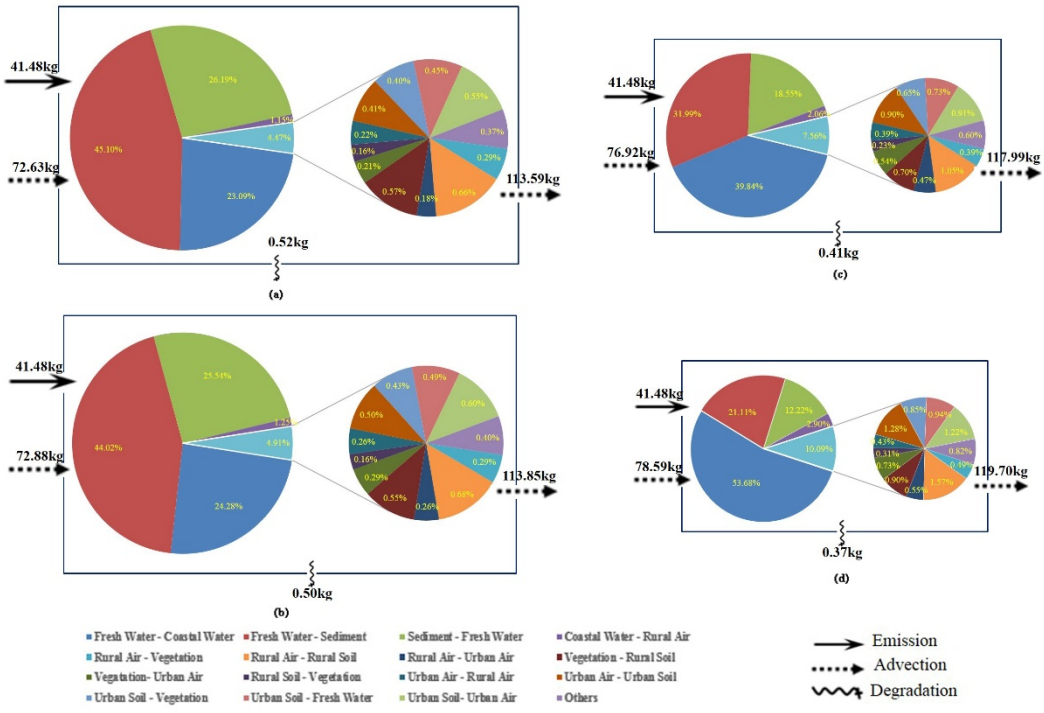

Fig. 5 The changes of PFOS fate and transportation of grid 26 under emission scenario 1 and moderate climate change scenario A1B : (a) baseline 2010; (b) 2016-2035; (c) 2046-2065; (d) 2081-2100.

In this part, we took grid 26 (containing the vast majority of Tianjin City) as an example to analyze the impacts of future climate change (scenario A1B) on the fate and transportation of PFOS in detail, including advection fluxes between adjacent grid (inflow/outflow fluxes of air), degradation rate, and intermedia transportation processes (Fig. 5). Under emission scenario 1, due to the increasing mean wind speed, both the inflow and outflow fluxes will increase, particularly

in the mid and late 21st century, by 5.91%, 8.21% for inflow flux, and 3.87%, 5.38% for outflow flux. For the not temperature dependent degradation rate, it will decline slightly with time. Because the degradation rate is a complex parameter, relating to the volume of each environmental compartment, PFOS concentration in each compartment, and the first-order reaction rate constant (Mackay, 2001; MacLeod et al., 2001). The value in Fig. 5 was the sum of all environmental compartments, hence, its reduction was maybe closely linked with the decrease of PFOS concentration in fresh water, fresh water sediment, urban soil, volume of rural soil, and rural air.

For the intermedia transportation processes, we could see that from fresh water to coastal water, fresh water to sediment, sediment to fresh water, and coastal water to rural air were the four predominant transfer ways among all transfer processes (Fig. 5). Among these four pathways, the transfer rate of fresh water to coastal water, coastal water to rural air increases over time, particularly for the former, from 1/4 of the total in 2010 to more than half in the late 21st century. It is because of increased runoffs from fresh water to coastal water led by more and more precipitation in the mid and later 21st century. For the transfer rate of coastal water to rural air, it is driven by temperature increasing volatilization. The transfer rate of the other two predominant pathways will reduce much in the future, especially in the mid and late 21st century, decreasing by 5.62% - 74.55% for fresh water to sediment, and 5.73% - 74.62% for sediment to fresh water, in the future (Fig. 5). According to the transfer principle between fresh water and sediment, along with the concentration reduction in fresh water, the concentration in sediment will also decrease, as well as the transfer rate between them.

4. Conclusion

This paper explored the potential integrative effects of future climate change and emission rate on the fate and transportation of PFOS in the Bohai Rim of China using BETR-UR model, taking the effects of urbanization into consideration at the same time. Our results suggested that wind speed, degradation rate, and intermedia transfer processes affect PFOS advection processes. Under the influences of climate change (including temperature, precipitation, wind speed, sea-level rise, and soil carbon stock) and urbanization, the projected concentrations of fresh water and urban soil would decrease a lot in the future, potentially lowering the exposure burden of biota

in fresh water and urban soil. These reductions were predicted to result from increased temperature, precipitation, and urbanization. While that of coastal water and rural soil displayed an opposite trend, which would bring out more adverse effects and risk on organisms, particularly for marine ecosystem. Besides, there were big influences of climate change on the mass fluxes of PFOS to the Bohai Sea. It is important to point out that these predicted changes would occur under BAU emission. However, through modern, effective chemical management practices and legislation, chemicals with PFOS-like properties might be effectively regulated and reduced, and then concentrations of PFOS in each compartment would sharply decline and lower the risk on ecosystems. It suggests that in the future emission reduction policy-making process, climate change mitigation and adaptation should be taken into serious consideration, as well as urbanization planning.

Acknowledgement

This study was supported by the International Scientific Cooperation Program with Grant No. 2012DFA91150, the National Natural Science Foundation of China under Grant No. 414201040045 and No. 41371488, and the Key Project of the Chinese Academy of Sciences under Grant No. KZZD-EW-TZ-12. We would like to thank the editors and reviewers for their valuable comments and suggestions.

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