Exploring the fate, transport and risk of Perfluorooctane Sulfonate (PFOS) in a coastal region of China using a multimedia model

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Abstract

Perfluorooctane Sulfonate (PFOS) and related substances have been widely applied in both industrial processes and domestic products in China. Exploring the environmental fate and transport of PFOS using modelling methods provides an important link between emission and multimedia diffusion which forms a vital part in the human health risk assessment and chemical management for these substances. In this study, the gridded fugacity based BETR model was modified to make it more suitable to model transfer processes of PFOS in a coastal region, including changes to PFOS partition coefficients to reflect the influence of water salinity on its sorption behavior. The fate and transport of PFOS in the Bohai coastal region of China was

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simulated under steady state with the modified version of the model. Spatially distributed emissions of PFOS and related substances in 2010 were estimated and used in these simulations. Four different emission scenarios were investigated, in which a range of half-lives for PFOS related substances were considered. Concentrations of PFOS in air, vegetation, soil, fresh water, fresh water sediment and coastal water were derived from the model under the steady-state assumption. The median modeled PFOS concentrations in fresh water, fresh water sediment and soil were 7.20 ng/L, 0.39 ng/g and 0.21 ng/g, respectively, under Emission Scenario 2 (which assumed all PFOS related substances immediately degrade to PFOS) for the whole region, whilst the maximum concentrations were 47.10 ng/L, 4.98 ng/g and 2.49 ng/g, respectively. Measured concentration data for PFOS in the Bohai coastal region around the year of 2010 were collected from the literature. The reliability of the model results was evaluated by comparing the range of modeled concentrations with the measured data, which generally matched well for the main compartments. Fate and transfer fluxes were derived from the model based on the calculated inventory within the compartments, transfer fluxes between compartments and advection fluxes between sub-regions. It showed that soil and costal water were likely to be the most important sinks of PFOS in Bohai costal region, in which more than 90% of PFOS was stored. Flows of fresh water were the driving force for spatial transport of PFOS in this region. Influences of the seasonal change of fresh water fluxes on the model results were also analyzed. When only seasonal changes of the fresh water flow rates were considered, concentrations of PFOS in winter and spring were predicted to be higher than that under annual average conditions, while the concentrations in summer and autumn were lower. For PFOS fluxes entering the sea, opposite conclusions were drawn compared to the concentrations. Environmental risks from the presence of PFOS in fresh water were assessed for this region through comparison with available water quality criteria values. The predicted concentrations of PFOS in the Bohai coastal region provided by the model were lower than the water quality criteria published by the United States Environmental Protection Agency and Chinese researchers, while the concentrations in more than 80% sampling locations exceeded the European Union Water Framework Directive Environmental Quality Standards values. Seasonal variations of flow rate might cause significant increase in environmental risks.

Keywords:

Perfluorooctane Sulfonate (PFOS); fugacity based gridded model; multimedia transportation; environmental risk; Bohai coastal region.

1. Introduction

Perfluorooctane sulfonate (PFOS) and related substances have been identified as global pollutants and have received increasing public attention in recent years. Due to their unique physical and chemical attributes, including chemical stability and surface tension properties, PFOS and related substances have been widely used in both industrial processes and domestic products (3M, 2000; Kissa, 2001). PFOS has been known to be extremely environmentally persistent, bioaccumulative, toxic and capable of long-range transport (Giesy and Kannan, 2001; 2002; OECD, 2002). In 2009, PFOS and related substances were listed in Annex B of the Stockholm Convention on persistent organic pollutants (POPs) (UNEP, 2009). Different from most of other POPs, PFOS has relatively high water solubility and exists predominately in the anionic form in solution. So far, PFOS and other perfluorinated compounds (PFASs) have been found widely distributed in rivers and oceans (Ahrens et al., 2009; Ahrens et al., 2011; Bao et al., 2010; Li et al., 2011; Pan and You, 2010b; So et al., 2004; Yang et al., 2011). Aquatic environments are thought to be the primary compartment for PFOS in the environment.

Since PFASs were first detected in human blood in 1968, considerable efforts have been made on PFOS to identify its sources, fate and effects. Most of the research has focused on detection methods and technologies (Kuklenyik et al., 2004; Van Leeuwen et al., 2006; Yamashita et al., 2004), exposure characteristics (Chen et al., 2011; Naile et al., 2010; Pan and You, 2010a; Taniyasu et al., 2003), bioaccumulation (Shaw et al., 2009; Shi et al., 2012a; Taniyasu et al., 2003) and toxic effects (Hoff et al., 2004; Ribes et al., 2010; Scialli et al., 2007). Nevertheless, limited attention has been given to the fate and transport of PFOS in multimedia environmental systems. The Berkeley-Trent (BETR) model, which was developed based on the concept of fugacity, can be used to predict the fate of spatially explicit emissions along with inter-compartmental transfer processes and fate processes such as sediment burial and degradation. The model has been successfully applied for a range of chemicals at continental and global scales, and has been used for predicting the fate of organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) and polybrominated diphenyl ethers (PBDEs) (Lamon et al., 2009; Liu et al., 2014; MacLeod et al., 2011; Prevedouros et al., 2004; Toose et al., 2004). However, it has not been applied to the simulation of PFOS on a regional scale. As mentioned previously, the partitioning behavior of PFOS in the aquatic environment differs from typical POPs (Higgins and Luthy, 2006) because of its specific physicochemical characteristics. Further, PFOS is not only emitted from the manufacture and use, but also from the release and subsequent degradation of perfluorooctanesulfonyl fluoride (POSF) based precursor compounds as well as related polymers (Ellis et al., 2004; Martin et al., 2005). The transport of these related substances should also be considered in the modeling processes. However, using models such as BETR for multiple species that are inter-related is challenging, and so for this study the focus had to be restricted to PFOS. Further model developments in the future are necessary to take into account the potential formation of PFOS from the release and subsequent degradation of polymers.

The Bohai Sea is the innermost gulf of the Yellow Sea on the coast of Northeastern China. The Bohai coastal area, which is usually considered as a combination of Bejing, Tianjin, Liaoning, Hebei and Shandong provinces and municipalities, is one of the most prosperous economic regions in China. A wide range of industries are distributed in this region, including textile treatment, metal plating, production of fire-fighting chemicals and semiconductor industries, some of which are associated with industrial sources of PFOS and related substances in China (Xie et al., 2013b). Moreover, the Bohai coastal area is one of the most populated and urbanized regions in China, where the emission of PFOS from domestic sources is expected to be considerable (Xie et al., 2013a). Therefore, this study was conducted to determine the fate and pathways of PFOS release from emission sources to the environment, predict the concentrations in various environmental compartments, and assess the potential environmental risks caused by PFOS in the Bohai coastal region.

In this study, the BETR model was employed to simulate the fate and transport of PFOS in the Bohai coastal region based on mass balance principles and the steady state hypothesis. As PFOS is a type of anionic organic compound which has both hydrophobic and hydrophilic functionalities (Brook et al., 2004), the sediment-water partition coefficient of PFOS can be affected by various important factors, including salinity which has been ignored in previous modeling research (Armitage et al., 2009; Schenker et al., 2008). Improvements were made to the calculation of PFOS partition coefficient in order to reflect the influence of water salinity on the sorption behavior. As PFOS has completely different solubility in fresh water and costal water, further changes were made to the model algorithms accordingly. Based on the methodology and emission inventory proposed by Xie et al. (2013a) and Xie et al. (2013b), spatially distributed emissions of PFOS and related substances in 2010 were estimated for this region. Four different emission scenarios were investigated in which a range of half-lives of PFOS related precursors were considered to ensure that PFOS emissions were effectively captured. Concentrations of PFOS in air, vegetation, soil, fresh water, fresh water sediment and coastal water were derived from the modified model under the steady-state assumption. Measured concentrations of PFOS in the Bohai coastal region around the year of 2010 were collected from the literature (Bao et al., 2009; Li et al., 2011; Lu et al., 2012; Pan et al., 2011; Shi et al., 2012; Sun et al., 2011; Wang et al., 2012; Wang et al., 2011; Yang et al., 2011; Yang et al., 2010; Zhao et al., 2013). The reliability of model predictions was evaluated by comparison with available measured data. Fate and transfer fluxes were also analyzed using model predictions, and the influence of the seasonal fresh water fluxes on the model results were also assessed. Finally, a preliminary risk assessment of PFOS in fresh water in the region was made by comparing model predicted concentrations with available water quality criteria values (EU, 2011; Giesy et al., 2010; Yang et al., 2014). As an exploratory study on modeling the fate and transport of PFOS at regional scale, this paper will present valuable experience for modeling other hydrophilic and nonvolatile organic pollutants. The model results also provide a emissions database for assessing the spatial distribution and potential impacts of PFOS in the Bohai coastal region.

2. Methods

2.1 Study area and model structure

In this study, the Bohai coastal region covering 36°N to 43°N latitude and 116°E to 124°E longitude was divided into 56 regions using a 1×1 degree grid (see Fig.1). The model follows mass balance concept and fugacity approach (Mackay, 2001), and comprises six connected compartments including air, vegetation, fresh water, fresh water sediment, soil and coastal water. These compartments were further divided into several sub-compartments, representing air, water, solid particles and biota respectively. The 56 sub-regions were linked by advection of air, fresh water and coastal water between adjacent segments. Water exchange between fresh water and coastal water in estuary regions was also considered, which was termed 'runoff water' in this model. More details about the model structure can be found in MacLeod et al. (2001) and Liu et al. (2014).

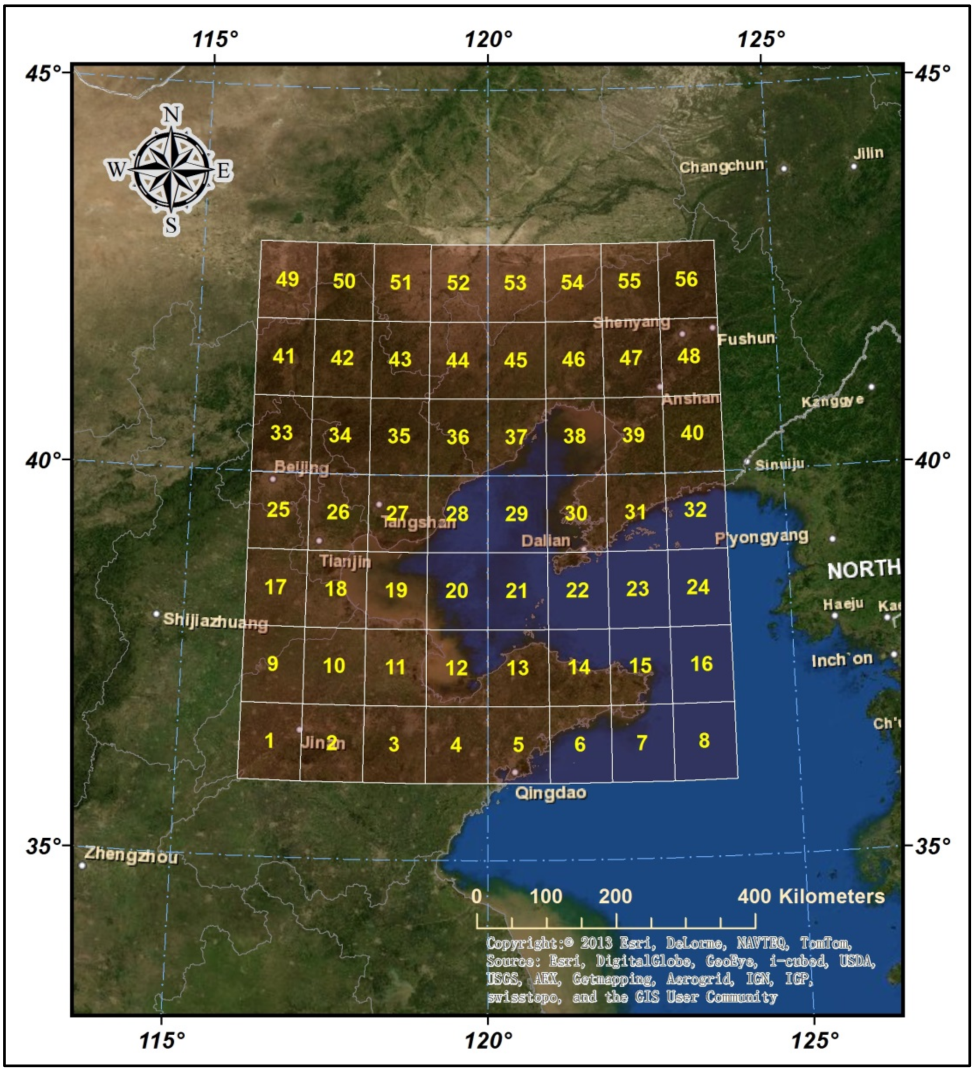

Fig.1. Location of study area and model segmentation.

2.2 Parameterization

In order to describe the fate of PFOS in a multimedia environment using the BETR model, three categories of parameters were collected: PFOS physicochemical properties, regional environmental features and air/water flux matrix parameters. Physicochemical properties of PFOS, including molar mass, melting point, solubility, vapor pressure, partitioning coefficient, half-life in multimedia and enthalpies of phase change, were mostly derived from 3M (2003) and Brook et al. (2004). There were 64 environmental parameters in total for each sub-region, describing the dimensions, composition and mass transfer coefficients in all environmental compartments. The meteorological and land cover data were collected from remote sensing and satellite datasets (Huffman et al., 2007; Los et al., 2000). Data for the flux matrix were collected and balanced for the air, fresh water and coastal water (Carton and Giese, 2008; Draxler and Rolph, 2013; MWR, 2006-2011; Saha et al., 2010). Further information on the parameterization of the model could be found in Liu et al. (2014).

Different from other existing POPs, PFOS is a type of anionic organic compound which has both hydrophobic and hydrophilic functionalities (Brook et al., 2004). The composition of PFOS makes its sorption and desorption behavior in sediment complex, consisting of several processes including hydrophobic interaction, electrostatic interaction and ion exchange. Therefore, the sediment-water partition coefficient (K_d) of PFOS can be affected by various factors, the most important of which are the organic carbon content (f_{OC}) of the sediment and salinity of water (S). It has been suggested that an increase in salinity can result in the enhanced sorption of

PFOS on sediment (You et al., 2010; Yu et al., 2009). In the Bohai coastal region, the salinity of river water in estuary regions is much higher than that in upstream regions as a result of the saltwater intrusion. Therefore a necessary improvement was made to the partition coefficient of PFOS in order to reflect the influence of salinity on the sorption behavior of PFOS. The organic carbon partition coefficient (K_{OC}) was derived using the following formula:

$$K_{OC} = K_d / f_{OC} \qquad (1)$$

Table 1. Measured K_{OC} values of PFOS in sediment.

Sample type	Location	n	log K_{oc} (L/kg)	Reference
Freshwater sediment*	USA	4	2.57 ± 0.13	(Higgins and Luthy, 2006)
Freshwater sediment*	Miyun Reservoir	3	3.08 ± 0.16 [2]	(Pan et al., 2009)
Freshwater sediment	The Netherlands	19	3.16 ± 0.28	(Kwadijk et al., 2010)
Freshwater sediment	Miyun Reservoir / Taihu Lake	15	3.10 ± 0.06	(You et al., 2010)
Freshwater sediment	Taihu Lake	22	2.88 ± 0.62	(Yang et al., 2011)
Freshwater sediment	Dianchi Lake	26	3.35 ± 0.32	(Zhang et al., 2012)
Coastal water SPM [1]	Tokyo Bay	6	4.8 ± 0.1	(Ahrens et al., 2010)
Coastal water sediment	Tokyo Bay	2	3.8 ± 0.1	(Ahrens et al., 2010)
Coastal water sediment*	Tokyo Bay	3	3.7 ± 0.56	(Ahrens et al., 2011)
Coastal water sediment	Dalian coastal area	5	3.47 ± 0.07	(Chen et al., 2012)

*: Artificial solution.

[1]: SPM: suspended particulate matter.

[2]: 3.25, 3.04, and 2.94 L/kg for aqueous concentration of 0.1, 0.5 and 1.0 mg/L.

Measured K_{OC} values of PFOS, in both fresh water and coastal water sediment are contained in Table 1. In addition, Chen et al. (2012) found that log K_{OC} increased linearly with the increase of log S. In this model, the value of log K_{OC} in fresh water sediment was set to 2.7, while in costal water sediment it was set to 3.7. The values of salinity of fresh water and coastal water were set to 0.032 and 32 (g NaCl in 1 kg water) respectively. Hence the revised K_{OC} of PFOS was calculated using the following formula:

$$\log K_{OC} = 2.7 + (1/3)\times\log(S/0.032) \qquad (2)$$

For each river, a length of 20 kilometers upstream from the estuary was set as the salt water intrusion area (Pan and You, 2010b) in which the salinity was assumed to increase linearly from 0.032 to 32. Salinity of water in each sub-region was calculated and introduced into the model. In addition, since PFOS exhibits completely different solubility in fresh water and costal water, the algorithms of the model were adjusted accordingly.

2.3 Emission scenarios

PFOS and related substances can be emitted into the environment during their whole life cycle, from production to consumption and waste disposal. Based on the methodology proposed by Xie et al. (2013b), emission of PFOS related chemicals from major related industries, including textile treatment, metal plating, fire-fighting and semiconductor industries, were estimated in the Bohai coastal area for 2010. The emission data were then distributed into each grid cell depending on the location of the plants. Domestic emissions of PFOS related chemicals derived from municipal wastewater treatment plant discharges were also estimated at the grid level, using a regression model of domestic emission density with population density and per capita disposable income (Xie et al., 2013a).

Three groups of PFOS related chemicals were taken into account in the emission estimation (Brook et al., 2004). The first group was PFOS-salts, including substances in the form of salts which are effectively PFOS itself. The second group included substances that can degrade into PFOS in the environment. These are considered to be potential sources of PFOS, and are termed PFOS-substances. Chemicals in the third group are PFOS related polymeric materials, termed PFOS-polymers, which can partially degrade into PFOS over the long-term. However, PFOS-polymers were not considered in this study as their half-lives may be more than 30 years (Brook et al., 2004). The degradation of PFOS-polymers can be neglected over the time interval considered in the model.

Although a large number of chemicals are included in PFOS-substances group, data on their properties are not available for the majority. In this study, N-EtFOSE (CAS 1691-99-2) was selected as model compound for this group, since it is most widely used and has the most extensive dataset. The properties of this compound were obtained from Brook et al. (2004). Model calculations were carried out with and without the inclusion of PFOS-substance in order to determine the possible contributions of PFOS-substances to the overall level of PFOS contamination. Different half-lives of PFOS-substances were also considered as they could vary greatly for different chemicals. On the basis of previous studies (Brook et al., 2004; Liu, 2008), four emission scenarios were selected for the model input:

1) PFOS-salts release only.

2) PFOS-salts plus PFOS-substances, assuming instant degradation to PFOS.

3) PFOS-salts plus PFOS-substances, assuming a 30.5 days half-life for degradation to PFOS.

4) PFOS-salts plus PFOS-substances, assuming a 1 year half-life for degradation to PFOS.

Based on the range of assumed emission scenarios, transport and fate of PFOS-substances in all the compartments and regions were predicted at steady state first. As a worst case, degradation of PFOS-substances was assumed to proceed to PFOS with no by-product, so that 1 kg/a (kilograms per year) of PFOS-substances were expected to generate 0.94 kg/a PFOS based on the ratio of molecular weight of PFOS and PFOS-substances. In this case, the degradation of PFOS-substances was converted into the emission of PFOS-salts and all added to the direct emission of PFOS-salts.

The estimated total emissions of PFOS and their compartment distributions for the different scenarios are shown in Fig.2. Compared with emission scenario 1, total emissions of PFOS increase by 14.97%, 14.56%, and 12.34% for scenarios 2, 3 and 4, respectively. Fresh water is the primary receiving compartment of emissions for all scenarios, although emissions to air increase for the last 2 scenarios as PFOS-substances are volatile and can be degraded in air. Spatial distributions of emissions were generally similar for each of the four scenarios, as illustrated in Fig.3. A possible explanation is that PFOS-substances and PFOS-salts were usually emitted in the same locations, and the quantity of PFOS-salts derived from degradation of PFOS substances is much smaller than that from direct emission. Therefore, the releases of PFOS-substances only affected local area emissions along with adjacent grid cells, but did not affect the wider distribution pattern of PFOS emissions. Fig.4.

shows the spatial distribution of PFOS emissions to air, soil and fresh water for emission scenario 2 (ES2). Similarly for all the three compartments, emissions in Weifang (sub-region number 4), Qingdao (sub-region number 5), Beijing (sub-region number 25 and 33) and Tianjin (sub-region number 26) are noticeably higher than for other regions.

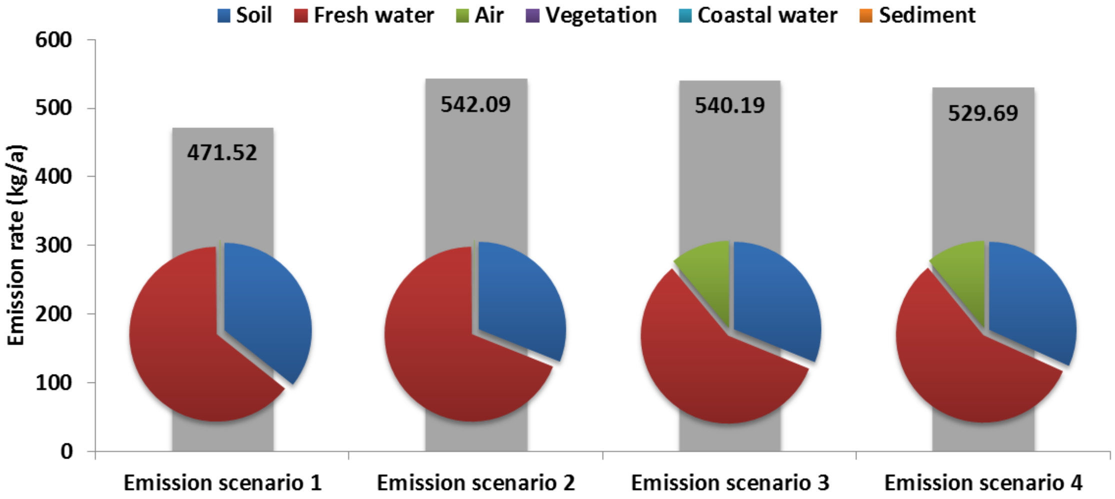

Fig.2. Integrated emissions of PFOS and compartment distribution for different scenarios.

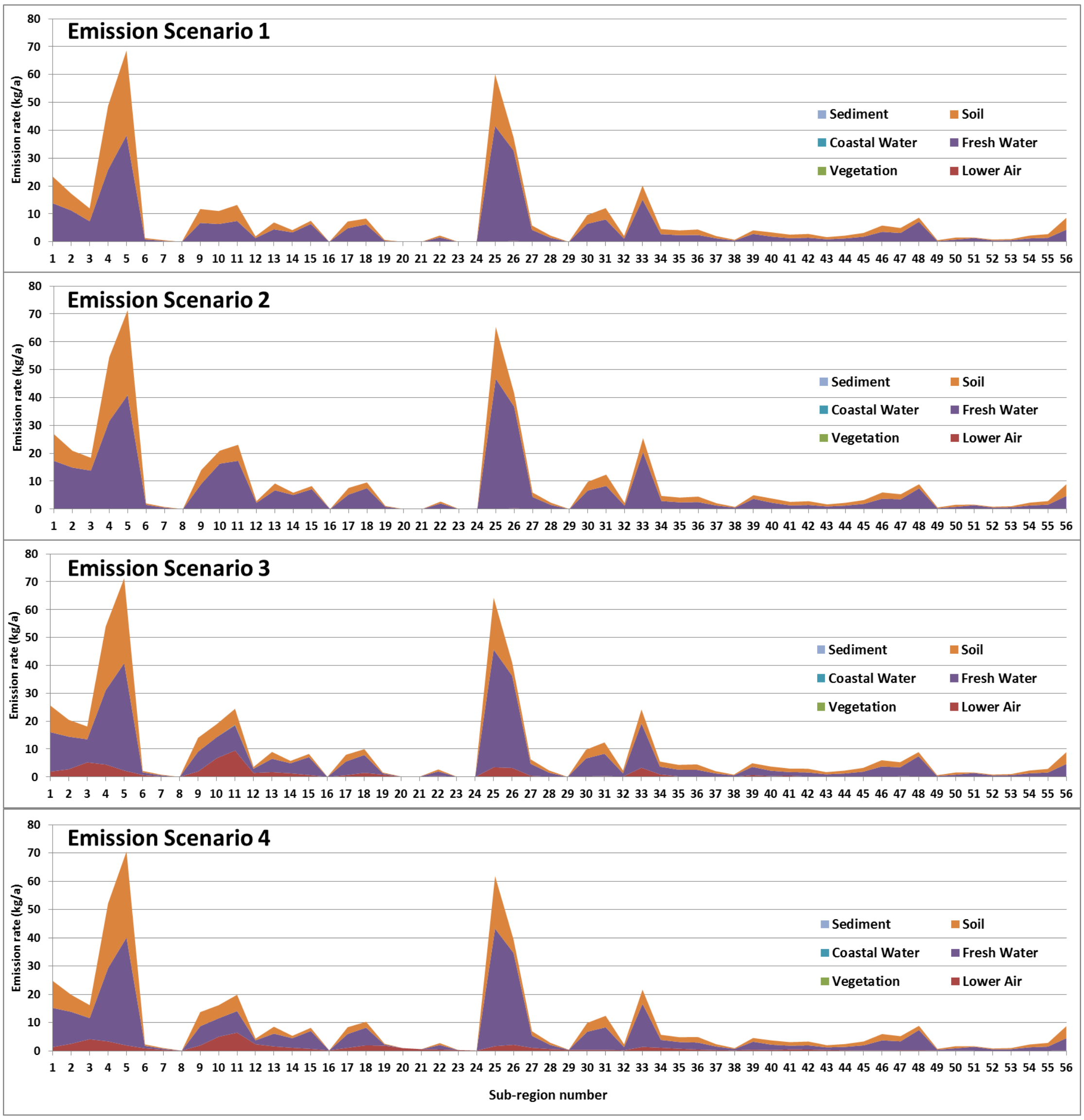

Fig.3. Emissions of PFOS in six compartments for different scenarios.

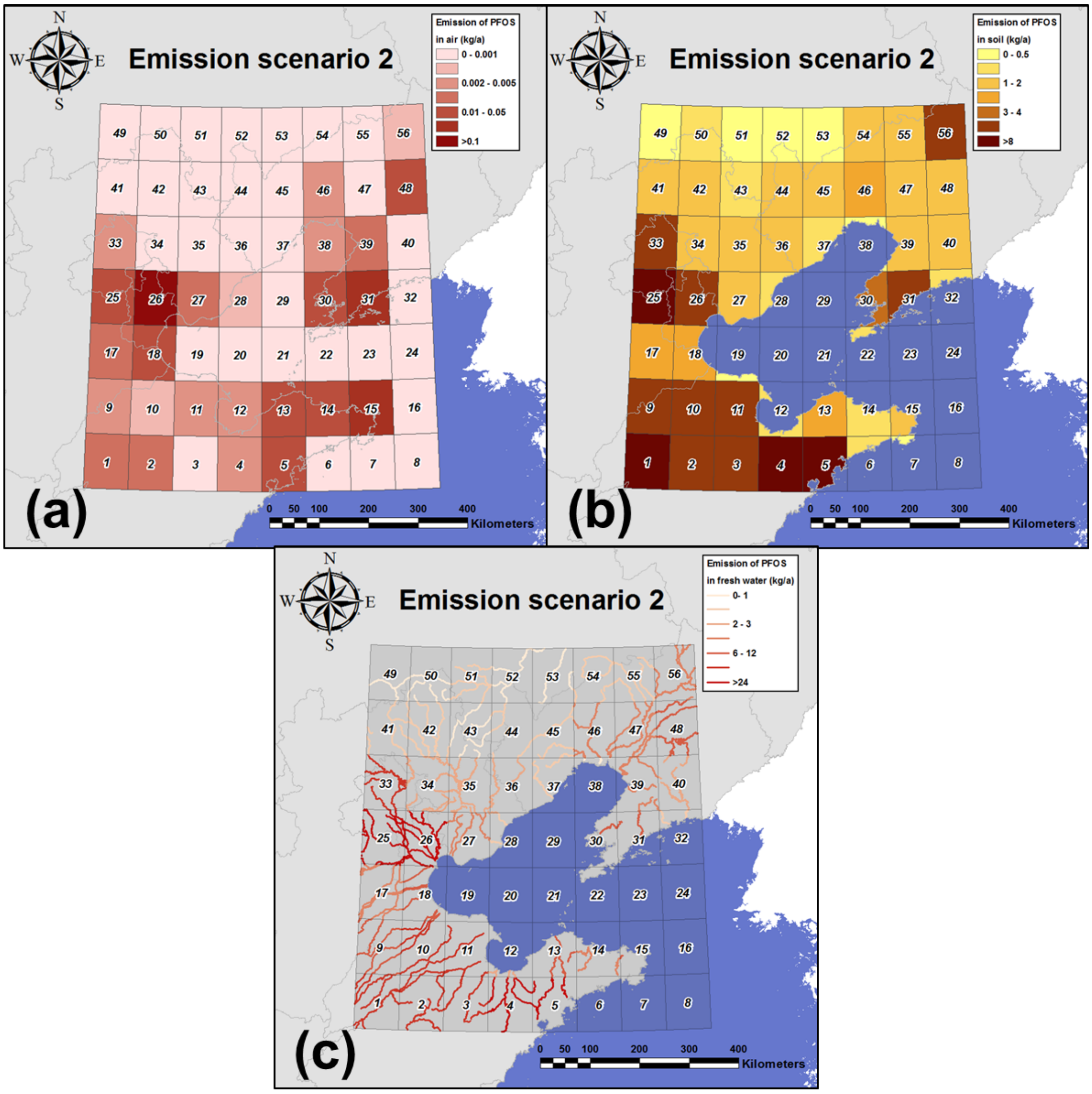

Fig.4. Spatial distribution of emissions of PFOS in air (a), soil (b) and fresh water (c) for ES2 in the Bohai coastal region.

3. Results and discussion

3.1 Model output and validation

The model was operated under steady state conditions for each emission scenario. Predicted concentrations of PFOS in fresh water, fresh water sediment and soil for each scenario are illustrated in Fig.5. In all compartments it was found that the predicted concentrations of PFOS for scenarios 1, 3 and 4 were similar, whilst the concentrations predicted for scenario 2 were slightly higher. The compartmental PFOS distribution patterns were similar to each other for each emission scenario. Regions predicted to have the highest concentrations were amongst the regions with the highest estimated emissions (e.g. sub-region 4, 5, 25, 26 and 30) but also included those downstream areas receiving PFOS burdens from the transportation by river water (e.g. sub-region 12). The median modeled PFOS concentrations in fresh water, fresh water sediment and soil were 7.20 ng/L, 0.39 ng/g and 0.21 ng/g, respectively, in ES2 for the whole region, whilst the maximum concentrations were 47.10 ng/L, 4.98 ng/g and 2.49 ng/g.

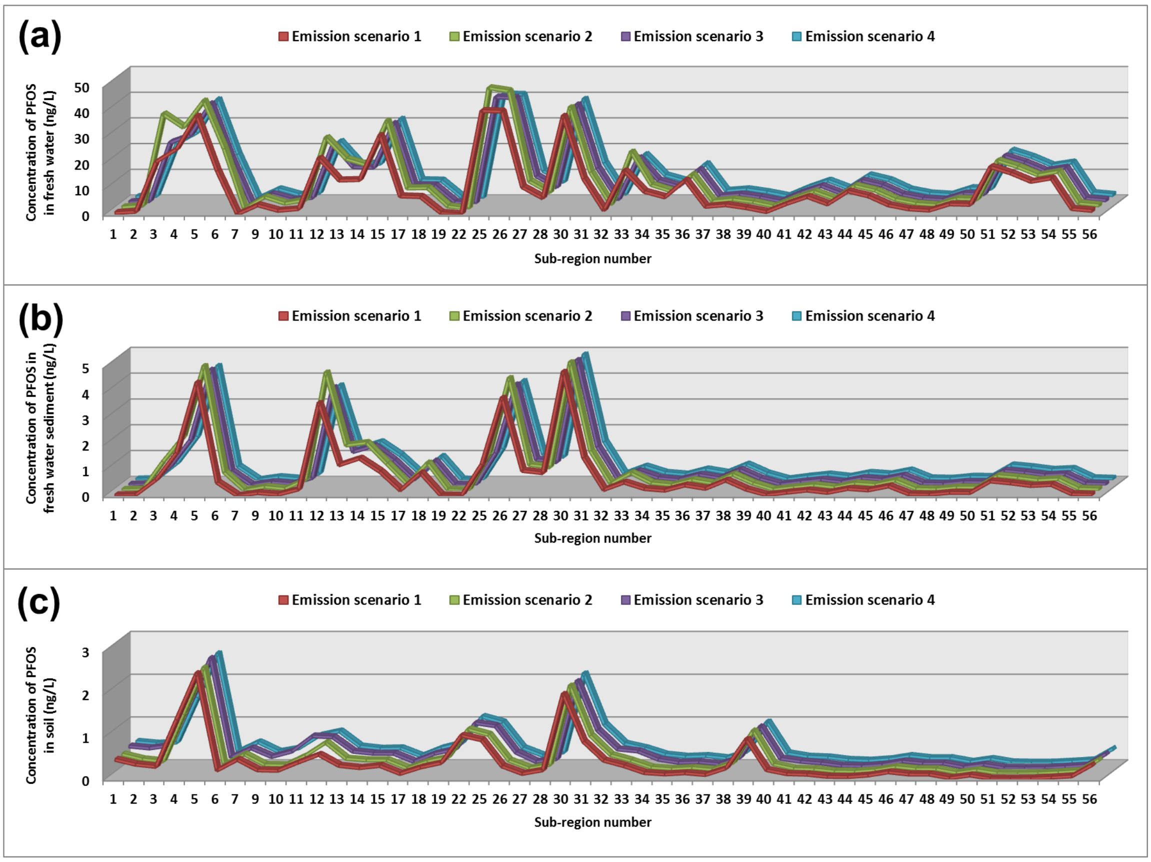

Fig.5. Concentrations of PFOS in fresh water (a), fresh water sediment (b) and soil (c) for different emission scenarios in the Bohai coastal region.

Measured concentrations of PFOS in samples from this region collected around 2010 were collated from literature sources (Bao et al., 2009; Li et al., 2011; Lu et al., 2012; Pan et al., 2011; Shi et al., 2012b; Sun et al., 2011; Wang et al., 2011; Yang et al., 2011; Zhao et al., 2013). These data were compared with predicted concentrations in all emission scenarios as a preliminary model evaluation (Fig.6). The range of modeled and measured concentrations generally agreed well for all three compartments.

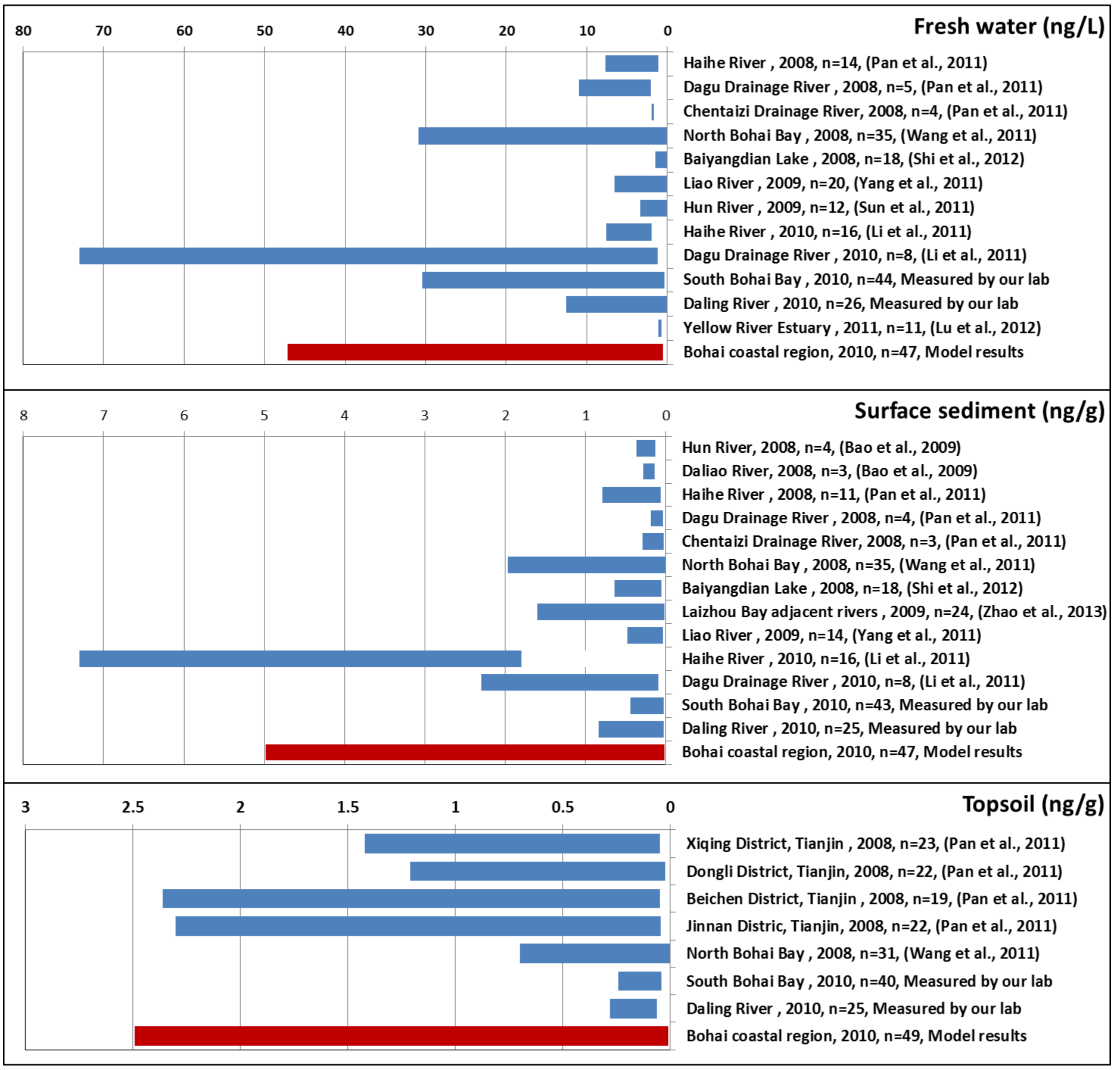

Fig.6. Measured and modeled concentrations of PFOS in fresh water, freshwater sediment and soil in Bohai coastal area.

3.2 Fate and transfer processes

As discussed previously, the predicted fate and behavior of PFOS is similar between the emission scenarios, therefore the results for ES2 have been taken as representative and discussed further. This includes data on the inventory in different compartments, sources of PFOS in soil and coastal water, advection fluxes and removal processes. In addition, since PFOS is usually considered as an 'untypical' POP owing to its physical-chemical characteristics and emission pathways, the model results of PFOS were also compared with those of BaP (Liu et al., 2014), a more 'classical' kind of POP, to explore the differences in their fate and transfer processes. The fate of PFOS in the Bohai coastal region was evaluated based on the predicted inventories in all the compartments, which are illustrated in Fig.7. Soil was the predominant sink of PFOS, in which 53% of the total amount of PFOS was stored. PFOS with a log Koc of approximately 3 adsorbs onto soil organic matter which reduces its ability to diffuse into other compartments, and it also exhibits low volatility. Nevertheless, the percentage of PFOS amount in soil was significantly lower than BaP, which was 95% according to Liu et al. (2014).

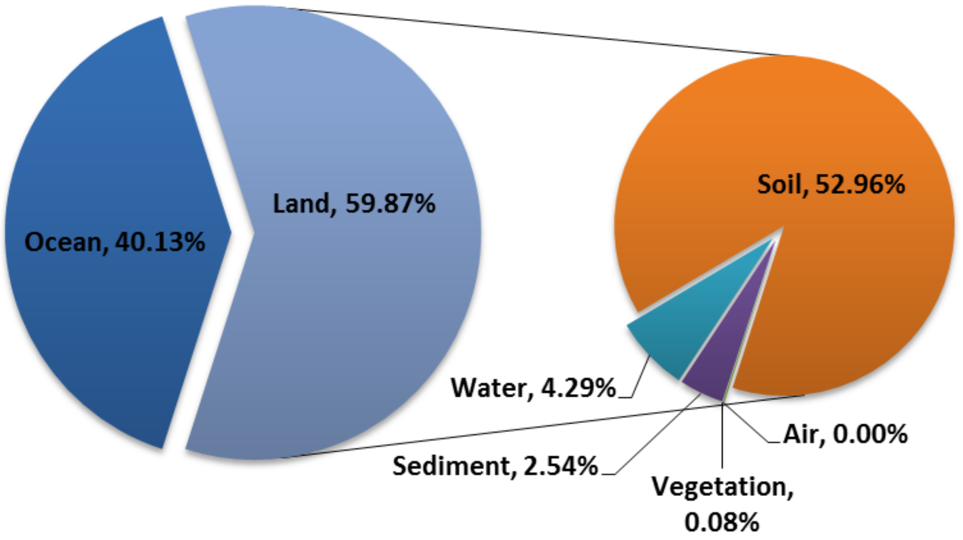

Fig.7. Compartment distribution of PFOS in the Bohai coastal region in ES2

The predicted percentage distributions of PFOS in coastal water, freshwater and fresh water sediment were 40.13%, 4.29% and 2.54%, respectively. This suggests that the total amount of PFOS stored in the aquatic environment was close to 50%, which is considerably higher than that for BaP (Liu et al., 2014). The discrepancy could be explained by the differences in emission and properties of chemicals. In ES2, 69% of PFOS was emitted into freshwater and transported within the aquatic environment. In addition, PFOS has a much higher aqueous solubility than BaP as it exists in aquatic environment in ionic state. Consequently compartments in aquatic environment become an important sink for PFOS.

Since more than 90% of PFOS were stored in soil and coastal water, the sources of PFOS in soil and coastal water were traced by calculating the PFOS fluxes entering soil and coastal water, which were shown in Fig.8 for soil and Fig.9 for coastal water. Under the assumptions of ES2, there were three main sources of PFOS to soil: (1) direct emissions; (2) diffusion, dry deposition and wet deposition from air; and (3) litter fall from vegetation. Fluxes of these 3 sources accounted for 78.86%, 14.20% and 6.94% of total fluxes, respectively, which implied that PFOS in soil mainly came from direct emissions. Furthermore, when considering the two main pathways for PFOS to enter coastal water, PFOS fluxes from rivers accounted for 88.26% of the total, which is considerably higher than that from air.

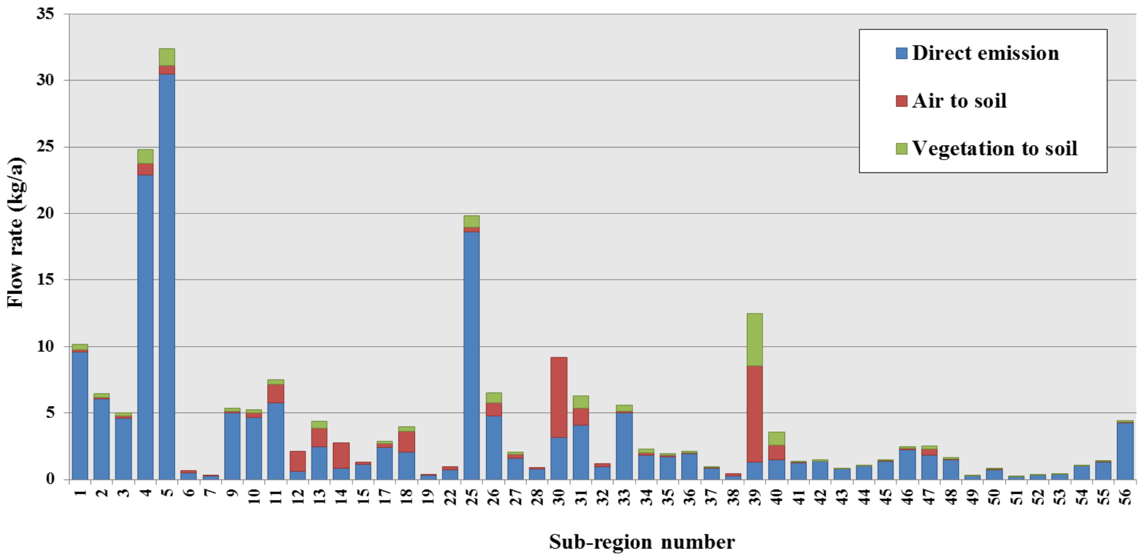

Fig.8. Sources of PFOS in soil in the Bohai coastal region

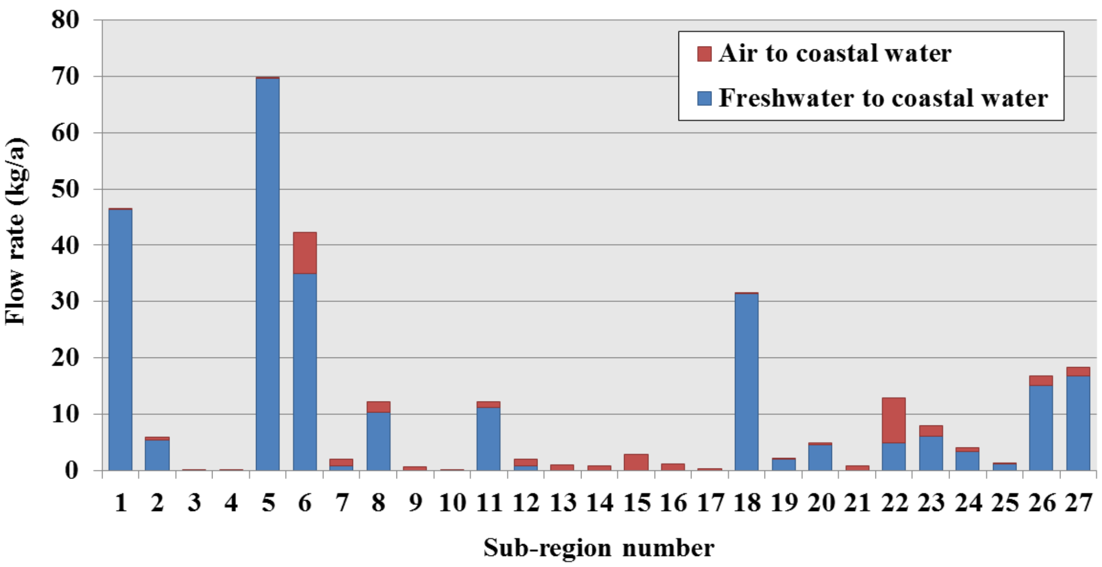

Fig.9. Sources of PFOS in coastal water in the Bohai coastal region

Advection fluxes of PFOS including inflow/outflow fluxes of air, freshwater and coastal water between different grid cells in the Bohai coastal region are illustrated in Fig.10. It is apparent that inflow/outflow of fresh water and coastal water were predominant pathways for spatial transport of PFOS in this region, while contribution of air flow was minimal. Water flow plays a crucial role in spatial transfer of PFOS, which is in contrast with that of BaP (Liu et al., 2014).

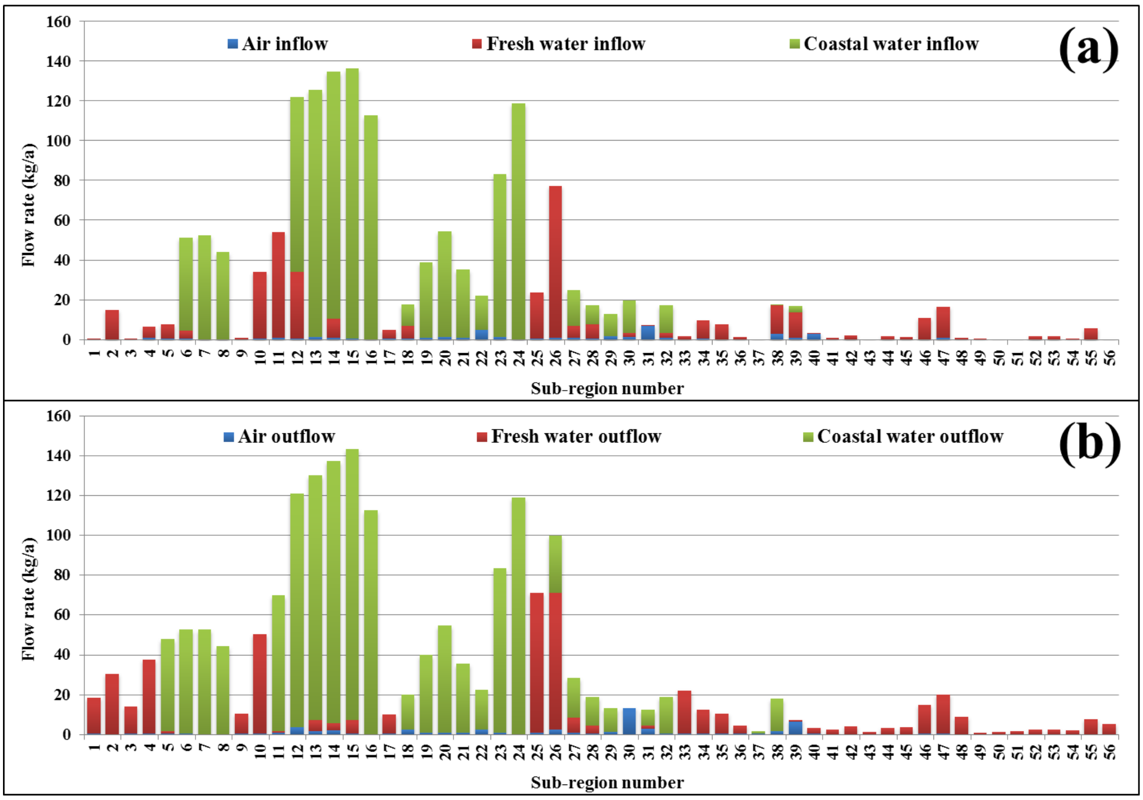

Fig.10. Spatial inflow (a) and outflow (b) of PFOS in the Bohai coastal region

The model predicts that PFOS would be primarily removed from the environment by advection and degradation processes. Advection processes include air outflow, vegetation growth dilution, fresh water outflow, coastal water outflow, leaching from soil and sediment burial. According to the model predictions advection fluxes account for 99.46% of the total removal fluxes of PFOS, and hence are the primary removal process in the Bohai coastal region. Since PFOS is thought to be a very stable chemical in the environment, it has extremely long half-life in soil and water and losses via degradation in the model are negligible.

3.3 Influence of seasonal variance of fresh water fluxes

From analysis above, it could be concluded that fresh water was not only the predominant receptor and sink of PFOS in environment, but also the driving force in

PFOS transportation. Hence a sensitivity analysis of all the parameters controlling concentrations of PFOS in fresh water was conducted, with sub-region 26 chosen as an illustrative example. For each model simulation, one parameter was selected and increased by 0.1%. The sensitivity coefficient of this parameter to the model output was defined using the following formula (3), where Y was set as the original model output concentration and $Y_{1.001}$ as the model output concentration with increased parameter:

$$S=(Y_{1.001} - Y) / 0.001 \times Y \qquad (3)$$

The results of sensitivity analysis indicated that emission quantity and fresh water flux were the most sensitive parameters, which might be the main source of uncertainty of modeled concentrations in fresh water. The surface water resources in the Bohai coastal region are scarce and significantly affected by precipitation. Fresh water fluxes vary considerably in this region because of seasonal changes in precipitation. Generally precipitation and fresh water flux in winter and spring are much lower than those in summer and autumn. In order to analyze influences of seasonal changes in fresh water fluxes on model results, monthly average fresh water fluxes in this region were collected (MWR, 2006-2011). Then seasonal average fresh water fluxes were calculated and put into the model, where March to May, June to August, September to November and December to February were defined as spring, summer, autumn and winter, respectively.

Model output concentrations of PFOS in freshwater with different seasonal average fresh water fluxes and annual average flow rates are shown in Fig.11. In general, when only seasonal change of fresh water flow rate were considered, concentrations of PFOS in winter and spring were higher than those calculated under annual average conditions, whilst concentrations in summer and autumn were lower. This could be attributed to the dilution of PFOS by fresh water as the emission flux in constant. It was also evident that the level of seasonal change varied greatly between sub-regions. In some sub-regions concentrations of PFOS changed exponentially, while in other sub-regions concentrations changed incrementally or remained unchanged. Negative correlations were found between the seasonal variation level of concentrations and the total fresh water fluxes (for a certain area equal to the sum of fresh water fluxes between adjacent areas and water discharged into the sea), as shown in Fig.11, which suggested that sub-regions with higher fresh water flux were less affected by seasonal change. It is likely that the water volume in water-rich areas was less affected by seasonal change of precipitation, and the concentration variances of PFOS were accordingly lower. On the contrary, precipitation was likely to be the main source of fresh water replenishment in water-deficient areas, and seasonal changes in precipitation rates might result in significant fluctuations in fresh water concentrations.

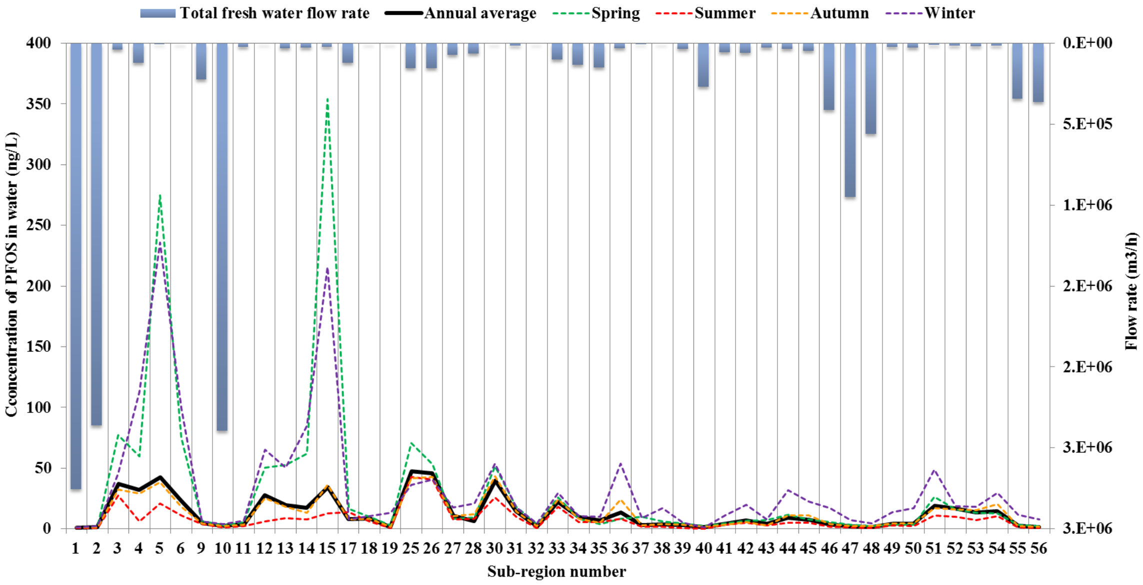

Fig.11. Seasonal variance of concentration of PFOS in fresh water in the Bohai coastal region

The influences of seasonal fresh water fluxes on PFOS fluxes entering the sea were also analyzed, as illustrated in Fig.12. In contrast to the concentrations, PFOS fluxes entering the sea in summer and autumn were generally higher than those under annual average conditions, while the fluxes in winter and spring were reduced. The results indicated that increase in water discharge lead to an overall increase of PFOS fluxes, although the concentrations decreased overall as a result of the dilution effect.

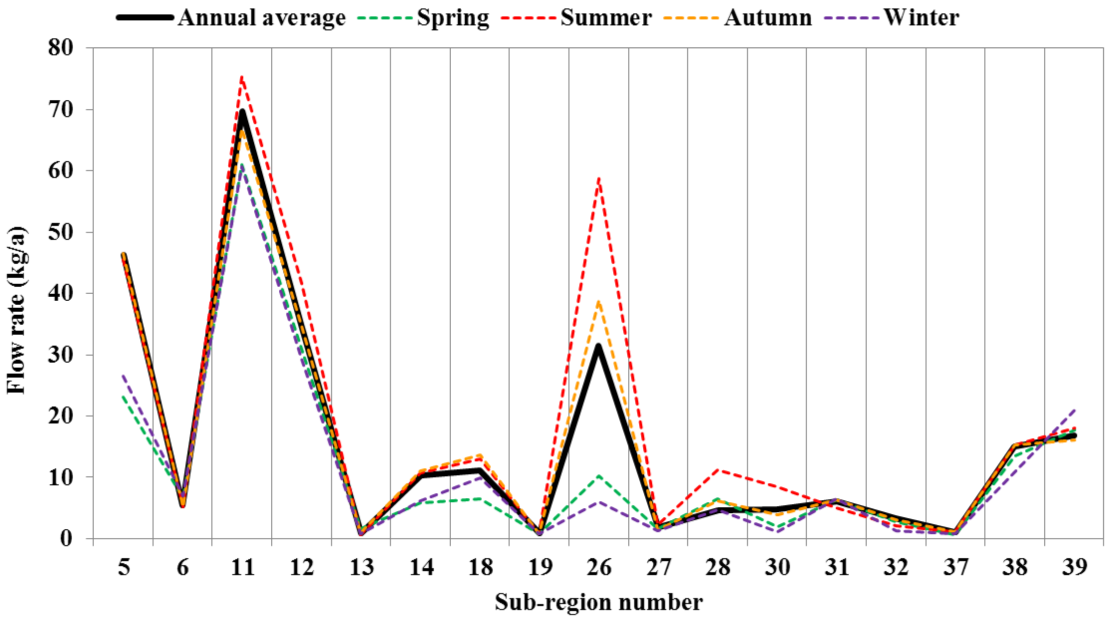

Fig.12. Seasonal variance of flux of PFOS entering the sea transported by runoff water

3.4 Environmental risks

The risks of PFOS on ecosystem and human health have been widely reported in recent years because of its wide-spread application in industrial processes and consumer products. Much of the current research on PFOS risk analysis has focused on aquatic ecosystems, as they are the main receptor and transmission pathway for PFOS (Naile et al., 2010; So et al., 2006; Steenland et al., 2009; Wang et al., 2012a; Wang et al., 2012b; Wang et al., 2011; Zhang et al., 2011; Zhang et al., 2012). In this study, the environmental risks of PFOS in this region were assessed by comparing the modeled concentrations with environmental quality criteria or standard values. Since official environmental quality criteria or standard values for PFOS are not available in China yet, several water quality regulatory guideline values, which are officially issued in foreign countries or proposed in research papers (EU, 2011; Giesy et al., 2010; Yang et al., 2014), were used for comparison in this study. The United States

Environmental Protection Agency (US EPA) divides water quality criteria values into criteria maximum (CMC) concentrations and criteria continuous concentrations (CCC), which are defined as the highest concentration of PFOS in surface water used to protect aquatic life from acute and chronic effects. The CMC (21 μg/L), CCC (5.1μg/L) and Avian Wildlife Value (AWV = 47 ng/L) for PFOS were first calculated by Giesy et al. (2010). A much tougher concentration limit for PFOS in surface water was set in the European Union (EU) Water Framework Directive (WFD) Environmental Quality Standards (EQS), which was 0.65 ng/L for annual averaged value (EU, 2011). Yang et al. (2014) have updated the CMC (3.78 mg/L) and CCC (0.25 mg/L) values for Chinese aquatic ecosystems, using the method recommended by the US EPA.

According to the model results using annual average fresh water fluxes, concentrations of PFOS in the Bohai coastal region for all the emission scenarios ranged from 0.53 ng/L to 47 ng/L. The modeled concentrations of PFOS were generally lower than the current CMC, CCC and AWV values, but more than 80% of the concentrations exceeded the EU WFD EQS value. Furthermore, it is worth noting that concentrations of PFOS in winter and spring went far beyond the EU WFD EQS value and AWV value in several sub-regions, which meant that seasonal variation of flow rates might cause significant increase of PFOS concentrations in surface water and hence environmental risk.

4. Conclusions

In this study, the BETR model was modified and further developed to simulate the fate and transport of PFOS in the Bohai coastal region. Spatially distributed emissions of PFOS and related substances in 2010 were estimated for this region with four different emission scenarios. Concentrations of PFOS in air, vegetation, soil, fresh water, fresh water sediment and coastal water were derived from the model under the steady-state assumption. Fate and transfer fluxes were analyzed based on the model results in ES2, in which all the PFOS-substances were assumed to be instantly degraded to PFOS, and influences of the seasonal change of fresh water fluxes on the model results were discussed. Environmental risks from the presence of PFOS in fresh water were assessed by comparison with available water quality criteria values. Overall, the results of this study indicated that:

- The total emissions of PFOS under the 4 scenarios were 470 kg/a, 540 kg/a, 540 kg/a, and 530 kg/a, respectively. Fresh water was the predominant receptor of emissions, which received more than half of the emissions in all the scenarios.
- The median modeled PFOS concentrations in fresh water, fresh water sediment and soil were 7.20 ng/L, 0.39 ng/g and 0.21 ng/g, respectively, in ES2 for the whole region, whilst the maximum concentrations were 47.10 ng/L, 4.98 ng/g and 2.49 ng/g, respectively. The ranges of modeled concentrations matched well with the available measured data.
- Soil and coastal waters were identified as the most important sinks of PFOS in the Bohai coastal region, in which more than 90% of PFOS was ‘stored’.

Nearly 50% of PFOS was stored in the aquatic environment, which was significantly higher than that for BaP. Flow of fresh water was found to be the driving force for spatial transport of PFOS in this region.

- When only considering seasonal changes of fresh water flow rate the, concentrations of PFOS in winter and spring were higher than those under annual average conditions, while the concentrations in summer and autumn were lower. Negative correlations were found between the seasonal variations in concentrations and total fresh water fluxes. For PFOS fluxes entering the sea, the opposite conclusions were drawn.
- The modeled concentrations of PFOS were generally lower than the current CMC, CCC and AWV values, but the concentrations in more than 80% of the sampling locations exceeded the EU WFD EQS value. Furthermore, it is worth noting that seasonal variation of flow rates might cause significant increase of PFOS concentrations in surface water and hence environmental risk.

The model results provide a source database for assessing the spatial distribution and possible impacts of PFOS in the Bohai coastal region. This paper also provides exploratory research on modeling the fate and transport of PFOS at regional scales, and will present valuable experience for modeling other hydrophilic and nonvolatile organic pollutants.

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