Urban and rural transport of semivolatile organic compounds at regional scale: A multimedia model approach

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ABSTRACT

Urban areas are generally regarded as major sources of some semivolatile organic compounds and other persistent organic pollutants (POPs) to the surrounding regions. Huge differences in contaminant emissions between urban and rural areas directly affect their fate in environmental media. Little is known about POPs behavior between urban and rural areas at a regional scale. A spatially resolved Berkeley-Trent-Urban-Rural Fate Model (BETR-UR) was designed by coupling land cover information to simulate the transport of POPs between urban and rural areas, and the Bohai Rim was used as a case study to estimate Polycyclic Aromatic Hydrocarbon (PAH) fate. The processes of contaminant fate including emission, inter-compartmental transfer, advection and degradation in urban and rural areas were simulated in the model. Simulated PAH concentrations in environmental media of urban and rural areas were very close to measured values. The model accuracy was highly improved, with the average absolute relative error for PAH concentrations reduced from 37% to 3% compared with unimproved model results. PAH concentrations in urban soil and air were considerably higher than those in rural areas. Sensitivity analysis showed temperature was the most influential parameter for Phen rather than for Bap, whose fate was more influenced by emission rate, compartment dimension, transport velocity and chemical persistence. Uncertainty analysis indicated modeled results in urban media had higher uncertainty than those in rural areas due to larger variations of emissions in urban areas. The differences in urban and rural areas provided us with valuable guidance on policy setting for urban–rural POP control.

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Introduction

In recent decades, contamination by persistent organic pollutants (POPs) has brought great concern from international environmental organizations, governments, academia, and the public. Assessment of the state and impacts of POPs is very important for environmental management, especially for regional ecological and human health risk management of POPs (Diamond and Hodge, 2007; Lindstrom et al., 2011). However, the availability of large-scale monitoring data in all environmental compartments (soil, water, vegetation, and air) is spatially and temporally limited. Therefore, application of multimedia fate models, which can simulate the concentrations, distributions, and persistence of chemicals in the environment based on mass balance equivalents (MacLeod et al., 2001; Liu et al., 2011, 2014), provides a useful tool for simulating the environmental behavior of chemicals.

Urban areas are generally regarded as major sources of some semivolatile organic compounds (SVOCs) and other POPs to the surrounding regions. These pollutants originate from, for example, production and use of chemicals, vehicle...
exhaust, and building materials. (Csiszar et al., 2014). Some chemical pollutant emissions (e.g., PAHs, PBDEs) in urban areas may be several times or even thousands of times higher than those in suburbs, which may lead to chemical concentrations in urban soil several times or even tens of times higher than in rural soil (Wang et al., 2010; Jiao, 2009). Hence, huge differences in contaminant emissions between urban and rural areas directly affect their fate in environmental media. However, little work has been related to the behavior of POPs between urban and rural areas at a regional scale (Csiszar et al., 2013). When the fate of chemicals has been simulated at a global or continental scale, the urban and rural areas were usually regarded as a whole. For example, the Berkeley-Trent fate model (BETR model) has been 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, 2004b), and global environment (Scheringer et al., 2000; MacLeod et al., 2005; Armitage et al., 2009). However, if urban and rural areas are taken as a whole at a regional scale, the differences in chemical behaviors between urban and rural areas cannot be well illustrated, and simulated concentrations in urban areas might be excessively undervalued due to the relatively high emissions in urban areas (Melymuk et al., 2011). Chemical concentrations that are not differentiated between urban and rural areas cannot really reflect the regional pollution level and ecological risk, especially for urban regions. Hence, modeling the interactions of POPs between rural and urban areas is important for the purposes of POP ecological risk assessment and control.

Models that can be used to simulate POP interactions between rural and urban areas are scarce. The Multimedia Urban Model (MUM) and Spatially Oriented MUM (SO-MUM) were used to simulate the fate of POPs from urban to suburban areas in Canada (Diamond et al., 2001; Csiszar et al., 2013). However, these two models focused on the intra-urban scale and the effects of impervious surfaces in urban area. Also, the BETR model is a spatially segmented multimedia model (Mackay, 1979, 2001) based on a fugacity model approach, which has been used to model chemicals including Toxaphene, PCBs, PAHs, PBDEs, and HCHs (MacLeod et al., 2001; Prevedouros et al., 2004a, 2004b; Toose et al., 2004). The BETR modeled result was the spatial average concentration in one sub-region, which may represent the average concentrations in various land use types such as urban land and farm land. Actually, the emissions of PAHs were considerably different between urban and rural areas (Shen et al., 2013). The BETR model application in the Chinese Bohai coastal region showed that the modeled concentrations of Benzo[α]pyrene (BaP) in air, fresh water, soil, and sediment generally agreed with field observations except for the soil concentration of urban areas, and the measured concentration of soil obtained from Beijing, one of the most developed cities in China, was 7 times higher than the modeled value (Liu et al., 2014). Due to the huge differences in PAH emissions between urban and rural areas, the results in urban soils were actually several times higher than in rural soils (Wang et al., 2010; Jiao, 2009). The factors affecting the fate of PAHs in urban and rural areas include emissions, vegetation cover, soil properties, and atmospheric aerosols. In particular, atmospheric aerosols in urban air were found to be a few times or even tens of times higher than in rural air (Mackay, 2001). So, it is necessary to consider the differences in the above parameters in the two areas.

Based on the steady-state BETR model, this study developed a spatially resolved multi-media BETR-Urban-Rural (BETR-UR) model, which took the effects of land uses 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 use, commercial land use, urban residential land use, municipal land for public facilities, and their buffers. In the rural areas, land uses include rural villages, agricultural land, grassland, forest land, rural residential land, unused land and so on (Wang et al., 2010). Moreover, the complex inter-media transport processes were optimized, distinguishing the emissions from urban and rural areas effectively. In this study, the coastal region of the Bohai Sea was selected as a case study for evaluating the model accuracy and adaptability, and for simulating the multimedia fate of PAHs (Benzo[α]pyrene and Phenanthrene, BaP and Phen) in environmental compartments.

1. Materials and methods

1.1. Description of optimized model structure

Within the original BETR model (MacLeod et al., 2001), a connected system of seven discrete and homogeneous compartments is considered as one segment (or grid). The seven environmental compartments contain upper air, lower air, vegetation, soil, sediment, fresh water, and coastal water. Full details for using the fugacity concept in contaminant fate models are available in the text by Mackay (2001). For a given region, the more segments are divided, the more complex the emission data and background information needed. Thus, under the original framework, a region is usually divided into a relatively small number of grids (e.g., <100) and a larger range (e.g., >10 km × 10 km) for describing national, provincial, or urban agglomeration scales. The simulated results of homogeneous soil and air in one cell were often unable to meet the needs of risk assessment, because huge variability between the urban and suburban areas was ignored.

Fig. 1 illustrates the nine compartments in the optimized BETR-UR model framework. In the BETR-UR model, the environment within each segment containing nine compartments is appropriate for distinguishing the urban and rural areas on a regional scale. The red arrows represent the added intermediary transfer processes (Fig. 1). Among those processes, the interactions between rural air and urban air are the most significant and need to be carefully considered. Although the processes of flow transfer and mass diffusion in segments or among segments may become complex, parameterization of urban areas is relatively easy. Specific environmental parameters include urban area, urban perimeter, urban-rural atmospheric mixing rate, vegetation coverage area, freshwater area of urban area, and particle fraction in urban air. Other parameters also could be edited if needed, e.g., water and solid runoff mass transfer coefficient (MTC), leaching from soil rate MTC, soil solid organic carbon, and volume fractions of soil water, air and solid.
The atmosphere contains a considerable amount of aerosols or particles that are important in determining the fate of certain chemicals. In a steady-state process, environmental media and emission estimates affect advection, degradation, diffusion rates of chemicals seriously. In the original simulation, a chemical (e.g., BaP) was assumed to directly discharge in the lower atmosphere (Liu et al., 2014). In the BETR-UR model, emissions should be estimated separately in the urban and rural areas. This paper will not focus on the discussion of chemical emission estimates, which are available from another publication (Shen et al., 2013). In addition, the parameters of advection rates (m³/sec) and diffusion MTC (m/sec) will affect the exchange ratios between rural and urban air.

1.2. Optimized modules of regional environment factors and contaminant fate

The delimitation of homogeneous urban areas in each segment is important for the model, and directly affects the average concentrations of contaminant in the urban area. Generally, the urban area in each segment can be estimated using a land use map from GIS, and buffer ranges should be set up to refer to environmental conditions and contaminant emissions and characteristics. Understanding the differences between urban and rural areas is crucial to determine the appropriate urban area (including buffer area). The relative differences could be represented by ratios of urban to rural concentrations (Harrad and Hunter, 2006). However, the ratios are discrete in terms of distance-concentration function depending on choice of sites, and urban–rural gradients can be better characterized using distance-dependent functions. Fig. S1 gives representative examples of distance-concentration relationships for air and soil. Usually, the buffer ranges of urban areas (or industrial areas) can be set from 0 km to 2 km for POPs such as PAHs, PCBs, and PBDEs (Fig. S1). In this study, the buffer range was set to be 2 km around urban and industrial regions, because some industries that were also important chemical emission points were located in suburbs. There may not be any urban area in some segments, and the model was designed to allow the selected urban area to be set to zero. The model does not allow urban air to be set to zero if urban soil is non-zero (or vice versa) in the same segment.

The Z value (mol/Pa/m³), which is specific to the capacity of a phase for a chemical, was derived according to Mackay (2001). The bulk Z values of rural air and rural soil were taken from the original equations and parameters, while urban air and urban soil are listed as follows:

Urban air : \[Z_{\text{urban}} = Z_{\text{a}} + Z_{\text{o}} \times \nu_{\text{Q}}\] (1)

Gas-phase : \[Z_{\text{g}} = 1/(RT)\] (2)
Fig. 1. New added equations are summarized as Eqs. (8)

\[
\text{Particles : } Z_d(8, 2) = 10^{(9.42 + 1.30 \times \log_{10} K_{oa})} \times Z_s(8, 1) \times \rho \times 10^5
\]

\[
\text{Urban Soil : } Z_s(9) = Z_s(9, 1) \times v_s + Z_s(9, 2) \times v_w + Z_s(9, 3) \times v_t
\]

\[
\text{Gas-phase : } Z_s(9, 1) = 1/(RT)
\]

\[
\text{Water in soil : } Z_s(9, 2) = 1/H = Z_{sub}(9, 1)/K_{sw}
\]

\[
\text{Soil : } Z_s(9, 3) = 0.41 \times K_{sw} \times Z_s(9, 2) \times f_{aw} \times \rho_p
\]

where \( R \) (8.314 Pa m\(^3\)/mol K) is the gas constant; \( T \) (K) is the absolute temperature; \( \rho_{oa} \) and \( \rho_p \) (kg/m\(^3\)), the density of aerosols and soil portions; \( v_s \), solid volume fraction; \( v_w \), air volume fraction; \( v_{oa} \), aerosol volume fraction; \( K \), partition coefficient; \( K_{oa} \), octanol/air partition coefficient; \( K_{sw} \), aerosol/water partition coefficient; and \( K_{aw} \), octanol/water partition coefficient.

Intermedia transport and transformation processes of chemicals between the nine compartments were quantified by D values (mol/Pa/hr), which were described in detail by Mackay (2001). Vegetation in the urban area was described using a modification of the approach of Cousins and Mackay (2001). Litterfall usually occurs, in which dead or decaying leaf matter falls from plant to the ground, and litter in urban areas is typically collected and disposed in a landfill or out of the city. This should be a permanent removal process for chemicals in the system, which do not include buffer regions. The contaminant process of wax erosion, whereby a portion of the leaf surface itself is physically removed, from vegetation to soil was considered (Mackay, 2001). A mass transfer coefficient, \( k_{sw} \) (m/h), is used to parameterize the leaf wax erosion rate. Mass balance equations can be assembled for each compartment using total D values for inter-compartmental processes Eqs. (8)-(18), and all the total D values that could be summed from D values for chemical transfer between specific compartments are shown in Fig. 1. New added equations are summarized as Eqs. (8)-(18), and the details of the main D value formulations specific to the BETR-UR model are available in Table S5. The unknown fugacity of the nine compartments would be solved analytically by matrix algebra using a Gauss elimination algorithm (Table S1). Concentrations, amounts and transport rates could be calculated, after estimates of fugacity for each compartment.

Urban air–Upper air : \( d(8, 1) = A(8, 1) \times k_{vertmix} \times Z(8) \)

Urban air–Rural air : \( d(8, 2) = A(8, 2) \times k_{UrbanAirmix} \times Z(9) \)

Urban air–Fresh water : \( d(8, 4) = A(8, 4) / (1/k_{ra} + Z_s(8, 1)) + 1/k_{ra} + Z_s(4, 1) \)

\[
+ A(8, 4) \times U_t \times Z_s(4, 1) + A(8, 4) \times v_s(8, 2) \times Z_s(8, 2)
\]

\[
\times v_p + A(8, 4) \times S_t \times v_s(8, 2) \times Z_s(8, 2) \times U_r
\]

\[
(10)
\]

Urban soil–Fresh water : \( d(9, 4) = A(9) \times k_{water} \times Z_{sub}(9, 1) + A(9) \times k_{soilrunoff} \times Z_{sub}(9, 3) \)

Urban soil–Urban air : \( d(9, 3) = A(9) \times Z_s(9, 1) \times A(9) \times Z_s(9, 3) \)

Urban soil–Urban air : \( d(9, 3) = A(9) \times (1/k_{ra} + Z_s(8, 1)) \)

\[
+ 1/k_{ra} \times Z_s(4, 1)
\]

Rural air–Urban air : \( d(2, 8) = A(2) \times k_{UrbanAirmix} \times Z(2) \)

Urban air–Urban air : \( d(8, 3) = A(8, 3) / (1/k_{ra} + Z_s(8, 1)) + 1/k_{ra} + Z_s(4, 1) + A(8, 3) \times U_r \times Z_s(8, 1) \times LAI \times f_w + A(8, 3) \times v_s(8, 2) \times Z_s(8, 2) \times U_r \times (1-f_w) \)

\[
\times v_p + A(8, 3) \times S_t \times v_s(8, 2) \times Z_s(8, 2) \times U_r \times (1-f_w)
\]

\[
+ A(8, 3) \times k_{water} \times Z(3)
\]

\[
(16)
\]

Urban Veg.–Urban soil : \( d(3, 9) = (1-f_w) \times A(9) \times U_t \times Z_s(4, 1) \times (1-f_w) + A(9) \times S_t \times v_s(8, 2) \times Z_s(8, 2) \times U_r \times (1-f_w) + k_{soilrunoff} \times Z_s(4, 1) + k_{soilrunoff} \times Z_s(4, 1) \)

\[
+ A(8, 3) \times k_{water} \times Z(3)
\]

\[
(17)
\]


where \( f_{oc} \) is the fraction for organic carbon; \( A \), the media interfacial areas (m\(^2\)); \( K_{oa} \), the aerosol/air partition coefficient; \( k \), the mass transfer coefficient (MTC), (m/sec); \( k_{oa} \), (m/sec), the air side MTC; \( k_{sw} \), (m/sec), the water side MTC; \( k_{water} \), (m/sec), water runoff rate from soil; \( K_{water} \), (m/sec), solids runoff rate from soil; \( k_{vertmix} \), (m/sec), upper and lower air mixing rate; \( k_{vertmix} \), (m/sec), vegetation take-up rate from soil; \( k_{UrbanAirmix} \), (m/sec), urban and rural air mixing MTC; \( k_{water} \), (m/sec), wax erosion rate; \( v \), the volume fraction; \( v_{water} \), water volume fraction; \( S_t \), the scavenging ratio; \( U_t \), (m/hr), the rain rate, \( U_r \), (m/hr), the dry deposition rate, \( f_w \), the canopy wet interception fraction; \( TSCF \), water phase concentration factor of transpiration; and LAI, leaf area index. More details are available in Table S5.

In the BETR-UR model, individual segments are linked by inter-regional flows of upper air, lower urban air, lower rural air, fresh water, and coastal water. These inter-segment connections are illustrated in Fig. 1. The movement of air and water transport is an important aspect in contaminant transport between regions. Compared with the original model, upper air and coastal water movement and the corresponding balances did not change, but the balance of lower air was changed into Eq. (20) (Table 1). Fresh water balance in each region is described as Eq. (21), which could play a more important role, especially in the case of relatively high amounts of water-soluble contaminants.

The transport of urban and rural air in the real environment is complex. The representations of urban and rural air in different segments have different spatial distributions on the map, which may directly increase the computing difficulty and affect the flow results. Urban area is disrupted by the physical nature of the urban environment, where surface roughness for wind flow may be higher than in the rural area. Csiszar et al. (2013) advised using a 100 m air compartment.
rather than varying the air concentration with height or for different areas for the SO-MUM model. In the BETR-UR model, the inter-regional movements of air are described by matrices of flow rate. Accurate estimation of the air flow balance is important for the simulation of chemical transport in the atmospheric medium. 24-hour trajectories for every 4 days in 2008 were obtained from the National Oceanic and Atmospheric Administration (NOAA) Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model [Draxler and Rolph, 2013]. The proportion matrices of air moving from one grid cell to adjacent regions were computed along the trajectories, and then corrected to achieve a flow balance using an iterative matrix technique [Liu et al., 2014]. We assumed that all the air compartments were based on the calculated air matrix and the same wind rate between urban and rural areas in the same segment, which may cause errors in advective losses, as horizontal wind speeds up in the urban areas. Fig. 2 shows the typical air advective exchanges between the urban and rural compartments. In the BETR-UR model, it is assumed that the air rates flowing out from i to j, m³/hr. G(i,j) could be estimated by mean wind velocity. The model did not distinguish different urban areas in the same segment, which means atmospheric exchange rates for different dimensions of an urban compartment were the same, so G(a,x) was used instead of G(a1,x) and G(a2,x). The outflow rate of i contains the outflow from urban air Ga(i,j) and from rural air Gr(i,j) (Eq. (23)). G(i,j) could be estimated by mean wind velocity. The contaminant mass leaving from i is calculated by Eq. (24), and D values were derived from Eqs. (24)–(26). Although the fugacity values of formula (27)–(28) were unknown, those could be calculated by the iteration algorithm in the model. The calculation method for mass flowing into j was similar to that for outflow from i.

### 1.3. Case study area and model setup

The Bohai coastal region, including part of the Bohai Sea and its surrounding area, is one of the most prosperous regions in China because of its coastal advantages. In this work, the study area included Beijing, Tianjin, Liaoning, Hebei and Shandong provinces and municipalities. Rapid economic development has caused a great increase in energy consumption and pollutant emission, leading to a series of ecological and environmental problems. A large amount of steel manufacturing and coking enterprises, the main emission sources of PAHs, are distributed in this region (Liu et al., 2014).

The longitude of the Bohai coastal region is from 116°E to 124°E, and the latitude is from 36°N to 43°N. It is divided into 56 grids of 1°×1° (Fig. 3). The land use types of the study area are also displayed in Fig. 3. Each grid contained 8 compartments, which were lower urban air, lower rural air, urban soil, rural soil, fresh water, fresh water sediment, coastal water, and vegetation. In this study, the effects of upper air were ignored, as the influence of long-range air transport within this region was considered to be limited.

### 1.4. Properties of PAHs

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds that have two or more than two benzene rings. They have received more attention because of their widespread

#### Table 1 - Flow balances of air and fresh water for region i among connected regions in the BETR-UR model.

Air balances:

\[
\sum_{j=1}^{n} (G(i,j)) = \sum_{j=1}^{n} (G(j,i)) \quad (19)
\]

\[
\sum_{j=1}^{n} (G(j,i)) + \sum_{i=1}^{n} (G(i,j)) = \sum_{j=1}^{n} (G2(j,i)) + \sum_{i=1}^{n} (G2(i,j)) \quad (20)
\]

Fresh water balances:

\[
\sum_{j=1}^{n} (G4(j,i)) + Rr(4) = \sum_{j=1}^{n} (G4(i,j)) + Lr(4) + Ev(4) + Wu(4) \quad (21)
\]

\[
G(i,j) \text{ Flow rate of upper air from i to j, m}^3/\text{hr.}
\]

\[
G2(i,j) \text{ Flow rate of rural air from i to region j, m}^3/\text{hr.}
\]

\[
G4(i,j) \text{ Flow rate of fresh water from region i to j, m}^3/\text{hr.}
\]

\[
G8(i,j) \text{ Flow rate of upper air from i to region j, m}^3/\text{hr.}
\]

\[
Rr(4) \text{ Rainfall rate to rivers and watersheds runoff rate in region i, m}^3/\text{hr.}
\]

\[
Ev(4) \text{ Evaporation rate from rivers in region i, m}^3/\text{hr.}
\]

\[
Wu(4) \text{ Water use rate for industry and agriculture in region i, m}^3/\text{hr.}
\]
existence and potential toxicity to living organisms. This study took BaP and Phen, two PAHs with priority for control listed by the US EPA, as simulation objects. The physical-chemical properties and suggested values of the PAHs at 25°C are shown in Table 2.

1.5. Emission estimation

The global atmospheric emissions of 16 PAHs at the country level for a period from 1960 to 2030 from 69 major sources were estimated by Shen et al. (2013), which were mainly from six sectors (energy production, industry, transportation, commercial building, agriculture, and natural sources). Regression models and a technology split method were used to estimate country- and time-specific emission factors (Shen et al., 2013). In that study, a 0.1°×0.1° gridded global PAH emission inventory was developed for 2007 and 2008 according to the corresponding global fuel consumption database (PKU-PAH-2007 and PKU-PAH-2008, where PKU stands for Peking University). A comparison with other studies indicated no systematic differences between the PKU-PAH inventory and those previously developed. In this study, emissions for urban and rural areas were calculated by multiplying the mean emission per unit area with the area of the region. It was estimated that the total emissions of BaP and Phen into air in 2008 in the study area were 213.43 t and 1,483.23 t, respectively, and the total emissions of BaP in lower urban air and lower rural air in 2008 were 117.81 t and 95.62 t, respectively. The total emissions of Phen in lower urban air and lower rural air in 2008 were 648.85 t and 834.38 t, respectively.

2. Results and discussion

2.1. Model validation and contaminant fate

Concentrations of BaP and Phen in all compartments were estimated by the BETR-UR model calculations under the steady state assumption. Model results were assessed by comparing simulated BaP and Phen concentrations with measured data in all the compartments in the Bohai coastal region (Table S2). Available measured data for PAH concentrations in the year of 2008 were collected from published sources (Jiao, 2009; Liu et al., 2010; Men et al., 2009; Peng et al., 2011; Shi et al., 2010; Wang et al., 2011; Zheng et al., 2010; Liu et al., 2011; Cai et al., 2011).

Fig. 3 – Case study area and land cover map.
unimproved model results was BaP emissions in the study area. The average relative error of an extremely inhomogeneous spatial distribution (requirement, but in some grids the measured data presented most measured data in the segments could meet the quality significant impact on the distribution of pollutants in the Source categories, both point and diffuse sources, will have a more data collected from diversified sources could improve the accuracy of spatial distribution of PAHs in our study.

Even though many measurement campaigns deliberately target the ‘hotspots’ of contamination, more data collected from diversified sources could improve the accuracy of spatial distribution of PAHs in our study. Source categories, both point and diffuse sources, will have a significant impact on the distribution of pollutants in the various media. Hence, we try to ensure uniformity of spatial data, and avoid using data influenced by a single point source. Most measured data in the segments could meet the quality requirement, but in some grids the measured data presented an extremely inhomogeneous spatial distribution (e.g., segment 38) or were lacking data in woodland and grassland (e.g., segment 37). The medians of the simulated data that were calculated separately by ArcGIS in urban and rural areas were used to validate the BETR-UR model. The data of measured and simulated Phen and BaP around the 1:1 line as shown in Fig. 4 show the viability and accuracy of the BETR-UR model in the Bohai coastal region. Compared with our previous results (Liu et al., 2014), PAH behaviors differentiated between urban and rural areas were simulated in this study, while Liu’s work mainly concerned the compartments as a whole. In addition, the relative errors (RE) between measured and simulated concentrations in most compartments became smaller (Table S2), which could be mainly attributed to the separate treatment of urban and rural areas in each compartment. Another reason may be that the estimated emissions adopted from the data by Shen et al. (2013) shown in Fig. 5 were nearly 2 times larger than Liu’s estimated BaP emissions in the study area. The average relative error of unimproved model results was –37% due to the huge impacts of urban emission, while that of the BETR-UR model was –3%. The BETR-UR model greatly increased the accuracy of contaminant fate, especially in a large proportion of the city area. Two main factors greatly impact the BETR-UR model accuracy. The first one is that the improved model separated emissions from urban and rural areas in each compartment, so estimated emissions in urban area would be more accurate, which could directly improve the modeling accuracy of PAH concentrations in urban areas. The second factor is that different parameter settings between urban and rural areas, such as vegetation coverage area, are key factors affecting the model results. For example, the relative error of BaP and Phen concentrations in soil in segment 26 obtained from an urban area of Tianjin City were –9.38% and –0.25%, respectively; those in segment 25 from an urban area of Beijing City were –34.08% and –9.26%, respectively.

Buffer ranges of urban areas could affect the simulated concentrations in soils. For example, Peng’s sampling sites (2011) were totally concentrated in urban areas, and no one site was located in a buffer zone. According to the distance-concentration relationship (Fig. S1), this may be the reason why simulated values in areas containing buffer areas were lower than measured values. In addition, the simulated BaP and Phen concentrations represented the average value in one sub-region, while the observed values were obtained at specific locations (Liu et al., 2014). The errors of the measured and simulated BaP and Phen concentrations could be attributed to the temporal and spatial variability of the environment. In segments 37 and 38, the number of monitored samples was not high enough for spatial representation, which might be the main reason for the large relative error. For example, in segment 37, woodland and grassland accounted for 30% of the

<table>
<thead>
<tr>
<th>Properties</th>
<th>Molar mass (g/mol)</th>
<th>Melting point (°C)</th>
<th>Aqueous solubility (g/m³)</th>
<th>Vapor pressure (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaP</td>
<td>252.32</td>
<td>175.00</td>
<td>0.00162</td>
<td>6.52E-07</td>
</tr>
<tr>
<td>Phen</td>
<td>178.23</td>
<td>101.00</td>
<td>1.15</td>
<td>2.50E-02</td>
</tr>
<tr>
<td>Properties</td>
<td>log(KOW)</td>
<td>log(KOA)</td>
<td>τ1/2-LUA (hr)</td>
<td>τ1/2-LUA (hr)</td>
</tr>
<tr>
<td>BaP</td>
<td>5.95</td>
<td>11.14</td>
<td>170 (100-300) a</td>
<td>170 (100-300) a</td>
</tr>
<tr>
<td>Phen</td>
<td>4.57</td>
<td>7.61</td>
<td>50 (30-100) a</td>
<td>50 (30-100) a</td>
</tr>
<tr>
<td>Properties</td>
<td>τ1/2 Veg (hr)</td>
<td>τ1/2 FW (hr)</td>
<td>τ1/2 CW (hr)</td>
<td>τ1/2 Sed (hr)</td>
</tr>
<tr>
<td>BaP</td>
<td>170</td>
<td>1704 (1000-3000) a</td>
<td>1704 (1000-3000) a</td>
<td>55,000 (&gt;30,000) a</td>
</tr>
<tr>
<td>Phen</td>
<td>550</td>
<td>550 (300-1000) a</td>
<td>550 (300-1000) a</td>
<td>30,000 (10,000-30,000) a</td>
</tr>
<tr>
<td>Properties</td>
<td>τ1/2 US (hr)</td>
<td>τ1/2 RS (hr)</td>
<td>E.P. (J/mol)</td>
<td>E.S. (J/mol)</td>
</tr>
<tr>
<td>BaP</td>
<td>17,040 (10,000-30,000) a</td>
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τ1/2-LUA: lower urban air reaction half-life.
τ1/2-LUA: lower rural air reaction half-life.
τ1/2-Veg: vegetation reaction half-life.
τ1/2 FW: fresh water reaction half-life.
τ1/2 CW: coastal water reaction half-life.
τ1/2 Sed.: sediment reaction half-life.
τ1/2 US: urban soil reaction half-life.
τ1/2 RS: Rural soil reaction half-life.

E.P.: enthalpy of vaporization from water to air, E. S.: enthalpy of solution from octanol to water.

a Half-life data of compartments were taken from Handbook of Physical-Chemical and Environmental Fate for Organic Chemicals (Mackay et al., 2001, 2006).
total land area, but only 4 sites were located around the coastal region. In segment 38, the tested mean concentrations of Phen in urban and rural areas were 67.28 ng/g and 55.84 ng/g, respectively, which were even larger than mean concentrations in industrial city areas (e.g., 26 and 27). Perhaps another reason was that Phen emissions in segments 37 and 38 were underestimated. Compared with simulated errors for BaP concentrations in air, soil and sediment, the variability of Phen errors were larger (Table S2). Phen emissions were much higher than BAP, and the half-life of Phen was shorter in various environmental compartments than that of BaP. For example, the suggested half-lives of Phen in air and soil were 55 hr and 5500 hr, respectively, but those of Bap were 170 hr and 17,000 hr, respectively (Mackay, 2001). Seasonal changes of Phen emissions were significant, and emissions in winter were significantly larger than other seasons (Shi et al., 2010) in the study area. All these factors may affect the predicted accuracy of Phen. In this case study, the parameters for the Phen half-life in air, soil and sediment were set to 50 hr, 8700 hr and 30,000 hr, respectively. The uptake of BaP and Phen by vegetation in urban and rural areas was also considered in this case study. However, due to the scarcity of measured...
Fig. 5 – Emission and simulated concentrations of Bap and Phen in air and soil in Bohai coastal region.
concentration data of BaP and Phen in vegetation, the model results were not validated by vegetation data.

The spatial distribution of BaP and Phen concentrations in air, soil and sediment is shown in Fig. 5. Compared with the emission data, the spatial distribution of BaP and Phen concentrations in air and soil was similar. However, the inter-compartment flow flux and that between segments led to changes in the spatial distribution from emission to ultimate fate. The average simulated concentrations of BaP in rural soil were 19.03 ng/g and 35.34 ng/g in the whole study area, while those in rural soil were 6.08 ng/g and 10.62 ng/g, respectively. BaP and Phen concentrations in urban soil were significantly higher than those in rural soil. Similarly, BaP and Phen concentrations in urban air were 2.55 and 17.28 ng/m³, while 0.54 and 7.63 ng/m³ in rural air. Concentrations in rural soil were 6.08 ng/g and 10.62 ng/g, respectively. BaP and Phen concentrations in urban soil were significantly higher than those in rural soil. Similarly, BaP and Phen concentrations in urban air were 2.55 and 17.28 ng/m³, while 0.54 and 7.63 ng/m³ in rural air. Concentrations in urban soil were higher in larger cities, such as Beijing, Tianjin, and Shenyang. Concentrations in rural air were higher in Beijing, Tianjin, Shenyang, and Tangshan, where emissions were larger. It could be inferred that the risky areas in terms of PAHs were narrowly distributed around the emission sources.

2.2. Transport fluxes of PAHs

The balanced transport fluxes of PAHs under steady state were calculated, including the intermedia transport flux in each grid, and inflow flux and outflow flux among adjacent grids.

2.2.1. Transport fluxes of BaP

The intermedia transport flux of BaP is shown in Fig. 6. Because each of these transport values was small and accounted for less than 1.00% of the total flux, we grouped all these processes together. Fig. 6 shows that the transfer process from rural air to coastal water was the major pathway for the majority of grids located beside the sea. In total, the flux of BaP entering into the Bohai Sea was estimated to be 13.98 ton/year, while the flux from air was 12.87 ton/year. The net flux from air to vegetation, soil, and fresh water was estimated to be 30.17, 141.82, and 4.12 ton/year, respectively. For most grids in the continent, transfer processes from rural air to rural soil, urban air to urban soil, rural air to vegetation, urban air to vegetation, and urban air to rural air were the five major pathways. Particularly for segment 22 including Dalian City, one of the most developed cities in China, the transfer flux from urban air to rural air almost accounted for half of the total flux. Compared to the process from urban air to rural air, the transport flux from rural air to urban air took up a smaller proportion. Hence, the effects on rural areas from urban areas cannot be ignored, and taking the interactions between them into consideration is essential. The results also showed that BaP entering the air compartment would be inclined to transfer into soil and vegetation, especially into the soil compartment. However, the flux from soil to air was much smaller. This was the main reason why the concentration of BaP in the soil compartment was higher. Fig. S2 shows the inflows and outflows of BaP among adjacent grids in the Bohai coastal region. The advection pathways connecting sub-regions were air, fresh water and coastal water. It was inferred that in the study area, the dominant driving force for spatial distribution of BaP was air; and in coastal areas, coastal water was also a main driving force. For segments 2, 10, 11, 46, 47, and 55, the Yellow River, Liaohe River and Daliao River played an important part in the spatial transport. The net transfer flux (NTF) of PAHs is a complex process involving the degradation and migration from each compartment. In this study, NTF was calculated by the difference between urban and rural air under the model in steady state conditions. The NTF of BaP from urban air to rural air was 16.2 ton/year in the whole study area, with an average of 0.33 ton/year in one segment (Table S4), which is significantly affected by the buffer range of urban areas.

2.2.2. Transport fluxes of Phen

The intermedia transport flux of Phen in the Bohai coastal region is shown in Fig. 6. The transfer process of Phen from air to coastal water was also a major pathway for the majority of grids. It was estimated that the total flux of Phen entering the Bohai Sea was 138.17 ton/year, while the flux from air accounted for 98.59%. In addition, the net flux from air to vegetation, soil, and fresh water was 49.72, 566.23, and 16.21 ton/year, respectively, which indicated that soil and coastal water were the final sink for Phen. The large flux between urban air and rural air reflected the huge advective exchanges between the two compartments, and lots of Phen emissions in urban area were transported through advective exchanges into other media. Compared with BaP results, the total flux of Phen in each grid was much larger than that of BaP, and the flux between vegetation and rural air took up a greater proportion for many grids, which may be caused by their different chemical properties, e.g., the value of Log(Koa) of BaP was higher than that of Phen.

Fig. S3 shows the inflows and outflows of Phen among adjacent grids in the Bohai coastal region. The major driving force for spatial distribution of Phen was air, and coastal water was also an important driving force. However, compared with BaP, Phen transport through fresh water accounted for a certain proportion in the advection processes (segments 2, 10, 11, 46, 47, and 55) because Phen has a higher solubility than BaP, demonstrating that the Yellow River, Liaohe River and Daliao River played an important part in the spatial transport. The NTF of Phen from urban air to rural air was 49.9 ton/year in the whole study area, on average 1.05 ton/year in one segment, which was higher than that of BaP (Table S4). The distribution of NTF shows distinct regional differentiation. The NTFs are relatively high in big cities including Beijing, Tangshan, Qingdao, Shenyang and Tianjin, which is closely related to the large emissions of Phen in these rapidly developed cities.

2.3. Model sensitivity and uncertainty analysis

Sensitivity analysis was used to test the sensitivity of the BETR-UR model by changing the parameter values to identify the most influential parameters for the model output. In this study, sensitivity analysis was performed for the new added parameters and original inputs that were the most sensitive parameters possibly controlling the PAH concentrations in air and soil, including the emission data and all model input parameters tested before (Liu et al., 2014). Each parameter was increased by 1.00% individually, and the sensitivity coefficient (S) was calculated (Table S3). The sensitivity and uncertainty analyses in one grid were conducted to represent the situation...
Fig. 6 – Intermedia transport flux of BaP and Phen in the study area. Note: others for BaP flux included the transport processes from rural air to fresh water, vegetation to rural air, vegetation to urban air, vegetation to urban soil, fresh water to rural air, fresh water to urban air, fresh water to coastal water, coastal water to rural air, rural soil to rural air, rural soil to vegetation, urban soil to vegetation, sediment to fresh water, and urban soil to urban air. Others for Phen flux included the transport processes from rural air to fresh water, urban air to fresh water, vegetation to urban air, fresh water to rural air, fresh water to urban air, fresh water to coastal water, rural soil to rural air, urban soil to urban air, rural soil to vegetation, urban soil to vegetation, and sediment to fresh water.
in the whole region, because all the input parameters in different grids were similar. Monte Carlo simulation was conducted to assess the uncertainty of prediction results based on the probability distributions of input parameters with Crystal Ball release 11.1.2.2 running in 64-bit Microsoft Excel 2010. Monte Carlo simulation was run 10,000 times repeatedly to obtain the distribution of the output. Key input parameters were selected for the uncertainty analysis according to the result of sensitivity analysis. Parameters were estimated by coefficients of variation (CVs) based on literature data. The values of the input parameters were selected randomly within their respective probability distributions.

Table S3 gives an example of BaP in segment 46 of the absolute values for the most sensitive parameters that controlled the concentrations in urban and rural media. The most influential parameters for the BETR-UR model outputs were emission rate, compartment dimension, transport velocity, and chemical persistence, which were similar with those of the original BETR model. However, emission rate and other parameters that were distinguished between urban and rural areas in the BETR-UR model displayed large spatial differences in parameter uncertainty. For example, urban emission and vegetation area were more influential for PAHs in urban soil and air than that in rural soil and air. The urban–rural air mixing MTC, one of the new added parameters, was also relatively sensitive for the model output, which could influence air flux between urban and rural areas. This parameter was difficult to measure, but could be calibrated in this model or estimated by an atmospheric transport model. In this work, the urban–rural air mixing MTC was suggested to be between 10–40 m/hr. Compartment dimensions including the sizes of total surface area, both urban and rural, may have a great impact on the model output. However, when the size of a compartment was changed in the model, other sensitive parameters in the compartment, for example emissions, also changed accordingly, which indicates that the relationships between parameters are complex and need to be explored further in future studies.

Urban buffer distance (indirect parameter) may also have a great impact on model output. The changes in urban buffer distance with GIS could affect the parameters, including urban area, rural area, vegetation area, fresh water area, and emission division in urban and rural area. Downscaling and more appropriate spatial resolution may further improve the model accuracy, but bring more difficulties in data collection, which is another important and challenging topic for further studies.

Table 3 shows the absolute values of Phen in segment 46 for the most sensitive parameters. Compared with the BaP sensitivity results, temperature was one of the most sensitive parameter affecting chemical distribution. Temperature changes may drive changes in environmental transport, resulting in remobilization or retention of contaminants from source regions (Paul et al., 2012). The predicted temperature sensitivity (e.g., the seasonal temperature changes) appeared to be large enough to alter the distribution of Phen, but not BaP. Seasonal variations led to parameter changes of temperature, rain rate, PAH emission etc., which could be sources of uncertainties in the model results. Because literature on the seasonal changes of PAHs emission was lacking, simulations were not carried out in this paper. However, the most sensitive parameters that varied with seasonal changes were considered to analyze the uncertainty of model results. All the distributions of prediction values fitted well with lognormal distributions according to comparison between the statistics of the fitted distributions and forecast values, as shown in Table 4. The CVs of BaP concentrations in urban air, rural air, urban soil, rural soil were 0.40, 0.34 0.54 and 0.46, respectively. It was inferred that the model output of BaP concentration in urban media had higher uncertainty than that in rural media due to the large variation of estimated emissions in urban areas and urban–rural flux. The CVs of Phen concentrations were larger than those of BaP, especially for the rural and urban soil, due to high sensitivity parameters, large variation of emission and reaction half-life.

3. Conclusions

A spatially resolved multi-media BETR-UR model coupled with land cover information was developed for simulating POPs behavior in urban and rural areas. The BETR-UR model, with each segment containing nine compartments, was used for a case study of the Bohai coastal region to estimate multi-media concentrations of PAHs. The processes of contaminant fate including emission, inter-compartmental transfer, advection and degradation in urban and rural areas were simulated in the model. PAH concentrations in urban soil and air were considerably higher than those in rural areas. The transport of PAHs between urban and rural air plays an important role affecting its fate in multimedia. Sensitivity analysis showed that temperature was the most influential parameter for Phen rather than for BaP, whose fate was more influenced by emission rate, compartment dimension, transport velocity and chemical persistence. Uncertainty analysis indicated that modeled results in urban media had higher uncertainty than those in rural areas due to larger variation of emissions in urban areas.

Simulated PAHs concentrations in environmental media of urban and rural areas were very close to measured values. The model could greatly improve the accuracy of the simulation results, with average relative error of –3 %, compared to –37 % for the original model. The BETR-UR model lays a good foundation to study the emission and transport of POPs between urban and rural areas. All the BETR-UR model results that were differentiated between urban and rural areas could be used as input to assess ecological or human risks of POPs at regional scale, which is valuable forpoDSicy making and implementation of urban–rural POPs control.

Acknowledgments

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### Table 3 – Sensitivity, coefficient of mean, standard deviation and variance of Phen for segment 46.

| Parameters                                      | $|S|$ of rural air | $|S|$ of Urban air | Mean   | CV  | SD  |
|-------------------------------------------------|------------------|-------------------|--------|-----|-----|
| Property temperature ($^\circ$C)                | 1.19             | 0.65              | 25.00  | –   | –   |
| Total surface area (km$^2$)                      | 0.73             | 0.84              | 9273.42| –   | –   |
| Enthalpy of vaporization (from water to air) (J/mol) | 0.63             | 0.34              | 78650.00| 6.6E–02 | 5.4E+03 |
| Rural emission (kg/y)                           | 0.59             | 0.05              | 1557.35| 0.47$^a$ | 7.24E+02$^a$ |
| Summer mean temperature ($^\circ$C)              | 0.50             | 0.30              | 21.7   | 0.05$^a$ | 1.09E+00 |
| Air half-life (hr)                               | 0.49             | 0.25              | 170    | 1.00$^c$ | 170.00$^c$ |
| Vapor pressure (Pa)                              | 0.35             | 0.19              | 0.03   | 1.30$^a$ | 3.25E–02 |
| Urban emission (kg/y)                            | 0.32             | 0.93              | 2524.31| 0.47$^a$ | 1.17E+03$^a$ |
| Rain rate (m/hr)                                 | 0.29             | 0.24              | 6.67E–05| 0.20$^b$ | 1.19E–05$^b$ |
| Rain scavenging ratio                           | 0.28             | 0.24              | 3.00E+05| 0.2$^b$ | 6.00E+04$^b$ |
| Volume Fraction Particles in air                | 0.23             | 0.16              | 5.00E–10| 0.43$^b$ | 2.17E–10 |
| Urban area (%)                                   | 0.13             | 0.36              | 13.60  | –   | –   |
| Aerosol deposition (m/hr)                        | 0.16             | 0.15              | 18.00  | 0.20$^b$ | 3.60 |
| Vegetation (%)                                   | 0.03             | 2.50E–3           | 75.00  | 0.10$^a$ | 7.50 |
| Urban–rural air mixing MTC (m/hr)                | 0.15             | 0.20              | 40.00  | 0.50 | 20.00 |

| Parameters                                      | $|S|$ of Rural soil | $|S|$ of Urban soil | Mean   | CV  | SD  |
|-------------------------------------------------|-------------------|-------------------|--------|-----|-----|
| Property temperature ($^\circ$C)                | 1.29              | 0.91              | 25.00  | –   | –   |
| Average soil depth (cm)                         | 0.97              | 0.97              | 10.00  | 0.35$^b$ | 3.50 |
| Soil Reaction half-life (hr)                     | 0.97              | 0.97              | 1.70E+04| 1.20$^c$ | 2.04E+04 |
| Density of soil solids                           | 0.80              | 0.80              | 2.40E+03| 0.06$^b$ | 1.44E+02 |
| Total surface area (km$^2$)                      | 0.73              | 0.84              | 9.27E+03| –   | –   |
| Enthalpy of vaporization (from water to air) (J/mol) | 0.68              | 0.48              | 78650.00| 6.6E–02 | 5.4E+03 |
| Summer mean temperature ($^\circ$C)              | 0.67              | 0.44              | 21.70  | 0.05$^a$ | 1.09E+00 |
| Rural emission (kg/y)                            | 0.59              | 0.05              | 1.56E+03| 0.47$^a$ | 7.24E+02$^a$ |
| Air Reaction half-life (hr)                      | 0.49              | 0.25              | 50.00  | 1.00$^c$ | 50.00 |
| Volume Fraction Particles in air                | 0.48              | 0.29              | 5.00E–10| 0.43$^b$ | 2.17E–10 |
| Vapor pressure (Pa)                              | 0.38              | 0.27              | 0.03   | 1.30$^a$ | 3.25E–02 |
| Aqueous solubility (g/m$^3$)                     | 0.38              | 0.27              | 1.15   | 0.20$^a$ | 2.30E–01 |
| Kow                                             | 0.38              | 0.41              | 6.67E–05| 0.20$^b$ | 1.19E–05$^b$ |
| Rain rate (m/hr)                                 | 0.36              | 0.40              | 3.00E+05| 0.20$^b$ | 6.00E+04$^b$ |
| Rain scavenging ratio                           | 0.35              | 0.00              | 2.52E+03| 0.47$^a$ | 1.17E+03$^a$ |
| Urban emission (kg/y)                            | 0.32              | 0.93              | 2.50E+03| 0.20$^b$ | 3.60 |
| Air in rural/urban soil                          | 0.31              | 0.31              | 0.20   | 0.20$^b$ | 0.04 |
| Water in rural/urban soil                        | 0.26              | 0.26              | 0.30   | 0.20$^b$ | 0.06 |
| Aerosol deposition                               | 0.21              | 0.20              | 1.80E+01| 0.20$^b$ | 2.50 |
| Urban area (%)                                   | 0.12              | 0.54              | 1.36E+01| –   | –   |
| Urban–rural air mixing MTC (m/hr)                | 0.15              | 0.20              | 40.00  | 0.50 | 20.00 |
| Urban vegetation (%)                             | –                 | 0.09              | 25.00  | 0.10$^d$ | 2.50 |
| Rural vegetation (%)                             | 0.05              | –                 | 75.00  | 0.10$^d$ | 7.50 |

$S = (Y_{1.001} - Y) / (0.001 \times Y)$, where $Y_{1.001}$ denoted the output of the model when the tested parameter $Y$ was increased by 0.10%.

$^a$ Zhang et al., 2007.

$^b$ Cao et al., 2004.

$^c$ Hauck et al., 2008.

$^d$ Los et al., 2000.

$^e$ Liu et al., 2014.

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**Appendix A. Supplementary data**

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jes.2015.12.005.

**REFERENCES**


Table 4 – Distribution of predictions of model uncertainty.

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