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Quantitative assessment of human health risks induced by vehicle exhaust polycyclic aromatic hydrocarbons at Zhengzhou via multimedia fugacity models with cancer risk assessment

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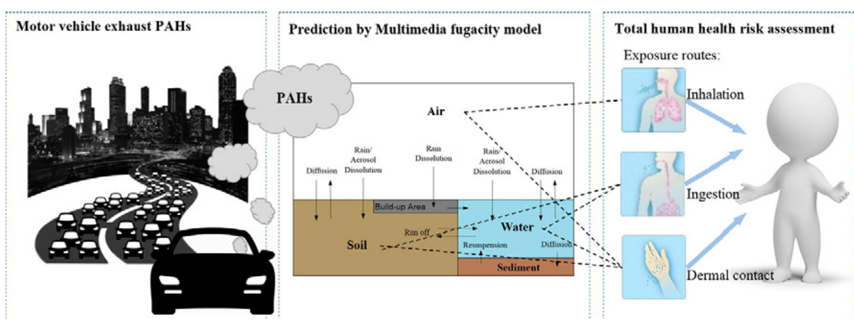
HIGHLIGHTS

- PAH emissions from vehicle exhaust are evaluated using multimedia models.
- The ILCR model was used to evaluate the cancer risk for residents of Zhengzhou, China.
- Dynamic fugacity model and ILCR models elucidated the health problems of residents.
- Health effects are estimated for increased concentrations of VEPAHs.

GRAPHICAL ABSTRACT



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ABSTRACT

Traffic-related pollution released a large amount of atmospheric polycyclic aromatic hydrocarbons (PAHs) which have severely influenced environmental safety and human health until now. However, the important issue of polycyclic aromatic hydrocarbon (PAH) emission from vehicle exhaust in urban populated areas has not been sufficiently investigated yet. This study focused on environmental behavior of vehicle exhaust PAHs (VEPAHs) and resultant health risk on local residents in urban populated areas. This study combined the multimedia fugacity models (Level III and Level IV) and the incremental lifetime cancer risk (ILCR) model, for analyzing the VEPAHs' environmental fate and related health risk on local residents in Zhengzhou of the central China. Regression models were applied to explore correlation between atmospheric concentration of VEPAHs and local pulmonary disease mortality rate. Our results demonstrate that the majority of VEPAH was sunk into the soil compartment in 2013, but the calculated BaP-equivalent concentrations of total VEPAHs in the air compartment exceeded the annual average standard limit of China (1 ng/m^3) yet. The human exposure routes of VEPAHs caused cancer risk in the following order: inhalation > dermal contact > ingestion.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of hydrocarbon organic compound with two or more aromatic rings, most of which are generated by incomplete combustion of organic substances (Liu et al.,

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2015b; Tobiszewski and Namieśnik, 2012). Some PAHs have strong carcinogenic, mutagenic, and teratogenic effects on human (Boström et al., 2002). Sixteen PAHs were selected for regulation by the U.S. Environmental Protection Agency (USEPA) due to their potential or identified carcinogenicity and genotoxicity (USEPA, 1992). The sixteen PAHs should be effectively controlled and monitored in the environment.

There are several sources that released PAHs into the ambient environment through diverse routes, including both natural and anthropogenic factors (Abdel-Shafy and Mansour, 2016). Since the Second Industrial Revolution, ever-increasing fuel requirement in industry, transport, and domestic heating emitted substantial atmospheric PAHs (Boström et al., 2002). Biomass combustion and traffic-related pollution were considered as major anthropologic sources of PAHs in the environment (Alves et al., 2017; Q. Wang et al., 2016; Y. Wang et al., 2016; Y.H. Wang et al., 2016). With recent urbanization in China, more and more vehicles are running in the urban areas. Vehicle traffic released a large amount of atmospheric PAHs and very likely increased health risk of local residents (Liu et al., 2015a; Q. Wang et al., 2016; Y. Wang et al., 2016; Y.H. Wang et al., 2016). Therefore, to assess the health risks of VEPAHs on local residents, it is necessary to predict accurate concentration of atmospheric PAHs, especially in downtown areas with large traffic loads.

Fig. S2 shows some relevance between vehicle population, concentration of $PM_{2.5}$ and lung cancer mortality rate in different provinces of China in 2008. The concentration of $PM_{2.5}$ was used to reflect the concentration of PAHs in this section because particulate matter is positively correlated with the concentration of PAHs based on reported works (Panther et al., 1999), especially VEPAHs (Dickhut et al., 2000). Fig. S2(a) shows the satellite-derived annual average $PM_{2.5}$ of China in 2008 gathered by the National Aeronautics and Space Administration (NASA). It clearly depicts the high concentrations of $PM_{2.5}$ in the central and southeast of China. Fig. S2(b) shows the vehicle population per km^2 of different provinces in 2008 and the higher vehicle density in the province near coasts. Fig. S2(c) illustrates the lung cancer mortality from Li et al. (2011) and a higher mortality was observed in the eastern China. From these figures, although it is hard to draw a conclusion that the increase in vehicle population causes the high concentration of $PM_{2.5}$ and finally leads to a higher risk of lung cancer, the relevant tendency promotes us to do this study. Due to severe air pollution and vehicle exhaust emission, the capital city of Henan province, Zhengzhou, was selected as the research area.

Due to persistency and semi-volatility of PAHs, once they are released into the environment, they would be transferred in and between environmental compartments via deposition (Feng et al., 2017) and diffusive exchange (McDonough et al., 2014), even transport over a long range (Lin et al., 2017; Mackay, 2001). Generally, PAHs gets widely distributed in air (Maliszewska-Kordybach, 1999), water (Huang and Batterman, 2014), and soil (Zhang and Fan, 2016) after they entered the environment. Many researchers developed models to describe the inherent distribution in multiple compartments and to predict the concentrations in different environmental media (Domínguez-Morueco et al., 2016; Vane et al., 2013). Several multimedia mass-balance models were used to predict concentrations of PAHs in air, water, soil, and sediment, including the Equilibrium Criterion (EQC) (Huang and Batterman, 2014), ChemCAN (MacLeod et al., 2002), and CalTOX (Loranger and Courchesne, 1997). All of these models were developed based on fugacity approach, which proved as an effective method to analyze chemical fate in the multi-compartments.

Multimedia fugacity models consist of four-level systems to evaluate the partitioning, diffusion, and transference of chemicals (the four types of fugacity models are listed in Supporting information (SI) Table S1). Levels I and II are suitable in an equilibrium multi-compartmental system. Level III involved compartmental-specific emission in steady-state open system, e.g., traffic-related pollution emitted atmospheric PAHs at a certain rate which were transported into other environmental compartments. Level IV added dynamics of emission and resulting temporal concentration course in non-steady open system. Huang et al. (2006) used the fugacity model to predict the concentration of PAHs and nitro-PAHs in Lake Michigan; in their study, the emission sources were attributed to traffic (53%), coal power plants (25%), coal-tar pavement sealants (15%), and coke ovens (7%). Xu et al. (2015) used the Level IV model to determine time trend of PAH concentrations in an industrialized city and the PAHs emission sources are considered from transportation and industry fuel consumption. These researches considered PAHs emission from various sources, but did not give enough attention to the influence of PAHs which are released from specific source, like vehicle exhaust. The VEPAHs from vehicle exhaust plays more detrimental role to urban residence health. Therefore, it is valuable to focus on vehicle exhaust emission as the source of PAHs in an urban city and to analyze the PAH partitioning between phases in detail. Here, the first aim of study is to use the multimedia fugacity Level III and IV models to predict concentrations of vehicle exhaust PAHs in a multi-compartmental environment of a specific urban area.

The second aim of this study is to establish the relationship between vehicle population and incremental human health risk of PAHs, and further to give the prediction of future ILCR trend. It is well-known that human is exposed to PAHs through intake and uptake, especially from the three major routes of inhalation, ingestion, and dermal contact. Xia et al. (2013) applied the ILCR model to achieve the goal of estimating the lung cancer risk posed by exposure to gas and particulate PAHs via inhalation during a human's lifetime. Xia et al. (2010) analyzed the ingestion lifetime health risks of PAHs as a function of exposure for different groups of humans. Wang et al. (2011) assessed the PAH-related health risks in urban surface dust encountered through dermal contact. It is worthy to note that the research mentioned above only focused on a unilateral pathway in the ILCR model. However, because of the wide spatial distribution of PAHs, human can be exposed to PAHs through multiple pathways. It is vital to understand exposure pathways and routes of PAHs sourced from traffic-related pollution after predicting the concentrations in multimedia. Here, the second aim of this study is to use multimedia (air, water, soil, and food) and multi-pathway (inhalation, ingestion, and dermal contact) ILCR models to assess human lung cancer risk to PAHs.

To estimate the influence of increasing vehicle population on the human health risks of local residents, the multimedia fugacity models (Level III and IV) and the incremental lifetime cancer risk model were performed. In this study, the main goals include 1) applying the multimedia fugacity Level III and IV models to predict the compartmental concentrations of sixteen VEPAHs with updated model parameters in Zhengzhou, 2) using ILCR model to evaluate the VEPAH-related additional cancer risk for humans in urban populated areas, and 3) establishing the regression model to express the correlation between atmospheric concentration of VEPAHs and local pulmonary disease mortality.

2. Materials and methods

2.1. Evaluation framework

Fig. 1 illustrates a general framework for analyzing environmental behavior of VEPAHs by the multimedia fugacity models and estimating human health risk of the VEPAHs using the ILCR model. First, the vehicle population data were collected to predict emission rates of VEPAHs into the air. The car population in 2012 was used to calculate the fixed emission rate; this value was then applied to the Level III model. Meanwhile, seventeen years of vehicle population data (1999–2015) were used to assess the time-dependent emission rate, which is applied to the Level IV model. Second, the model calibration method was carried out to optimize the model parameters to conform to realities situation of the study area. Then, the calibrated multimedia fugacity models analyzed the environmental behavior of VEPAHs based on the calculated emission rate. Next, to estimate the additional lifetime cancer risk of VEPAHs,

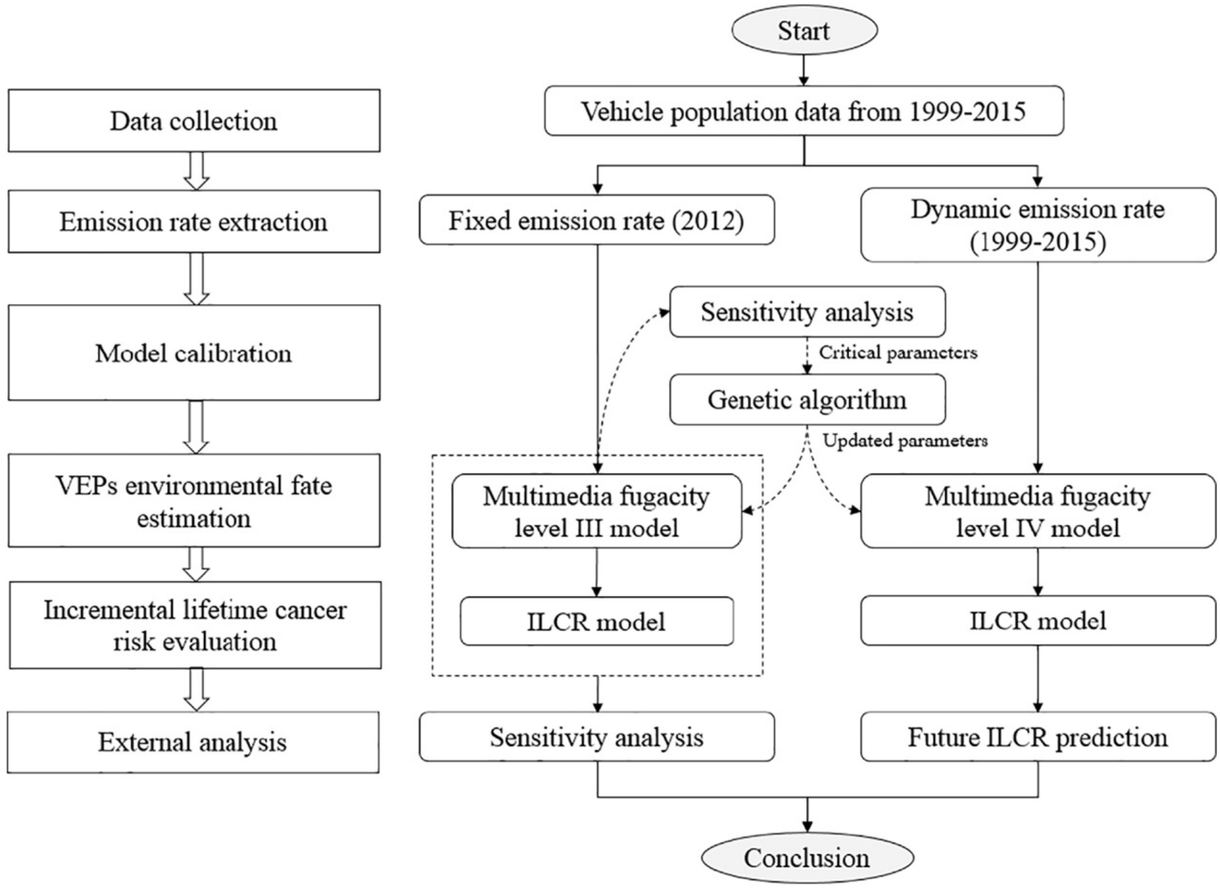

Fig. 1. Framework for predicting the environmental behavior and health risk of VEPAHs.

the predicted VEPAH concentrations in each phase were applied to the ILCR model. In this part, four VEPAH sources (air, water, soil, and food) and three exposure routes (inhalation, ingestion, and dermal contact) were considered. Finally, the sensitivity analysis of the Level III–ILCR model was carried out to evaluate the most relevant model parameter as well as its influence on the cancer risk assessment. Based on the Level IV–ILCR model, a prediction of future risks posed by VEPAHs on human health was given, based on the historical ILCR results. Furthermore, the relationship between the estimated ILCR value and the observed pulmonary disease mortality rate were determined.

2.1.1. Estimating emission rate of VEPAHs

Motor vehicles exhausts are assumed to be released only into the air, so only the emission rate of airborne VEPAHs needs to be considered. Vehicle properties affected the emission of VEPAHs, such as vehicle type population, and annual average mileage as well as fuel types. Many researchers found that diesel vehicles emitted more pollutants than gasoline vehicles (Gertler, 2005; Reşitoğlu et al., 2014), especially PAHs (Chang et al., 2009; Khalili et al., 1995). In this study, vehicles were divided into two categories according to fuel type (e.g., diesel vehicle and gasoline vehicle). Approximately 90% of heavy-duty vehicles (HDVs) and 5% of light-duty vehicles (LDVs) were diesel-driven and the remaining belonged to gasoline vehicles (DaheWebsite, 2017; Zhang, 2015; Zhao, 2014). LDVs consisted of three sub-groups, namely private cars, commercial cars, and freight cars. Alternatively, HDVs consisted of two sub-groups (coach/bus and freight car). The vehicle population data were extracted from Zhengzhou Statistical Yearbooks (1998–2015). Annual mileages (in Table S5) and emission factor of VEPAHs (in Table S6) from literatures (Ho et al., 2009) were provided in support information. The emission rate was calculated by Eq. (S1) in the SI.

2.1.2. Estimation of environmental behavior of VEPAHs using multimedia fugacity models

Compared to the Level I and II models, the Level III and IV models are more realistic and believable when analyzing the fate of chemicals because they assume that each phase has its own fugacity (i.e., a non-equilibrium system) and give more reliable descriptions of the chemical behavior during degradation, advection losses, and intermedia transport processes. The mass balance equations (Eq. (S2)) for Level III and IV models are listed in the SI as well as the D-value of adventive, reaction and diffusive process in SI, as shown in Eqs. (S3)–(S5).

Since the build-up area accounts for 33.27% proportion in the target research area (Zhengzhou), the characteristics of an urbanized area were considered in the modified fugacity models. The artificial impermeable surface in a build-up area could interdict the rain deposition process of pollutant transfer between air and soil compartments. Additionally, some pollutants would be deposited on the build-up area by rain; these would pass through sewage system into reservoirs or rivers, leading to the increasing pollutant transfer between the air and water phases (Xu et al., 2015). Therefore, in this study, the diffusive process of pollutants from air to water should add an additional mass transport process that corresponds to the amount of pollutants in the air phase droplets in the build-up area that are deposited by rain; this is calculated by Eq. (S6) in the SI.

In this study, sixteen EPA priority PAHs were selected as target compounds, including naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorine (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo[α]anthracene (BAA), chrysene (CHR), benzo[*b*]fluoranthene (BBF), benzo[*k*]fluoranthene (BKF), and benzo[α]pyrene (BAP), indeno[1,2,3-*cd*]pyrene (IcdP), dibenzo[*a*,*h*]anthracene (DBA), and benzo[*g*,*h*,*i*]perylene (BghiP). The observed concentrations of these VEPAHs (in Table S4) were lower than the concentration of air components (Logan, 2012), which is at low level in the environment regards to the limit in the linear function. Thus gaseous concentrations can be assumed to be linearly related to their fugacity (Mackay, 2001). Therefore, multimedia fugacity models were implemented to estimate the environmental behaviors of VEPAHs. Physical-chemical properties of VEPAHs are listed in Table S7 of the SI.

2.1.3. Calibration of the multimedia fugacity model

Environmental fate of pollutants is intimately connected with their physicochemical properties as well as environmental properties in specific study areas, so the model input parameters need to be updated when analyzing different chemicals in different study areas (Gouin et al., 2013; Mackay et al., 2014). Unfortunately, due to the barrier of accurately quantifying model input parameters, such as chemical emission rates to the four phases, the compartment dimension, transport velocity, it is hard to update model parameters in a specific area due to the number of dataset for parameters estimation was sparse. In this study, the sensitivity analysis and genetic algorithm based model calibration method was implemented to improve the performance of multimedia fugacity model based on the standard air phase VEPAHs concentration (SAC) measured in 2012 (Wang, 2015; Zhang et al., 2016). More details on the calibration method are shown in the SI. The updated parameters gathered from calibration method applied to the fugacity models to get the predicted VEPAH concentrations.

2.1.4. Evaluation of the incremental lifetime cancer risk (ILCR)

To estimate the incremental cancer risk of VEPAHs during human lifetime, the VEPAH concentrations from the multimedia fugacity models were applied to the ILCR model. Because VEPAHs were discharged into the atmosphere, they would become widely spread throughout the environment; human individuals exposed to the VEPAHs via various media (air, water, soil, and food) and through multiple pathways (dermal contact, inhalation, and ingestion) and the ILCR equations are shown in Eqs. (S7)–(S11) of the SI. PAHs in food could come from various sources, including raw food PAHs (such as VEPAHs sorped into food) and food-cooked PAHs, which were generated when food was cooked in high temperature or from incomplete combustion of cooking fuels. In this study, fishes were considered as the main source of food exposure because they were the most common foods that contained high concentrations of PAH (Bansal and Kim, 2015).

The dynamic ILCR was calculated with the dynamic VEPAH concentrations, which were estimated by the Level IV model. Based on the lasting 17 years of evaluated ILCR values, a prediction of future ILCR values (for 10 years) was carried out by the Oracle Crystal Ball software (Oracle Corp., Redwood Shores, CA) with a double exponential smoothing method.

2.1.5. Statistical analysis

The calculation of Level III–ILCR and Level IV–ILCR model were carried out with Matlab R2013b (MathWorks Inc., Natick, MA). The emission rate of Level III model was estimated based on the vehicle population reported of Zhengzhou in 2012. Background concentration in air phase was considered as the 87% of SAC in the Level III model, where the coefficient is assumed by the ratio between VEPAHs emission rate in 2011 and 2012. For the Level IV model, the time-trend emission was calculated by fitting a quartic function. The observed emission rate and the fitted curve of BaP are shown in Fig. S1 in the SI. The coefficients of the time-trend emission rate were calculated by the function of 'polyfit' in the Matlab listed in Table 1 and coefficients of determination (R^2) were above 0.98. To solve the set of ordinary differential equations in the Level IV model, stiff solver 'ode15s' in Matlab was used.

2.2. Study area

Zhengzhou is the capital city of Henan province, which is located on the southern bank of the Yellow River, and is a well-known major transportation hub in the east-central China (Fig. 2). As a core city in the Central Plains Economic Zone of China, the registered population of Zhengzhou caught up to 9.57 million before the end of 2015 (Statistics Bureau of Zhengzhou, 2015). As the development of city, the environmental problem is becoming increasingly obvious. As reported in China Environmental State Bulletin, the air quality index of Zhengzhou is in the bottom ten among 74 major city in china. Meanwhile, the total amount of the civil vehicle is increased 6.8 time in the last 10 years (Statistics Bureau of Zhengzhou, 2015). Due to industrialization and urbanization, environmental pollution in Zhengzhou is concerned. Meanwhile, a large quantity of PAHs has been released into the environment through traffic-related pollution. Therefore, this study focused on the downtown of Zhengzhou which has large traffic flows and high population density. Table S11 shows the compartment dimensions of the study field, including the area (Statistics Bureau of Zhengzhou, 2015), depth (Mackay, 2001), and volume. As a rapidly growing city, government only takes into account the economy-environment coordinate scheme to achieve sustainable development of Zhengzhou city.

3. Results and discussion

3.1. Calibration of multimedia fugacity model

The degradation half-life time (hfa) and depth of air in each VEPAH – Level III model were found to be the most influential among total thirty-four parameters in model according to Monte Carlo simulation

Table 1
Polynomial regression parameters of sixteen VEPAHs with the coefficients of determination (R^2).

VEPAHs	b1	b2	b3	b4	b5
NAP	-1.08×10^{-20}	4.05×10^{-15}	-4.35×10^{-10}	1.92×10^{-05}	1.28×10^{-01}
ACY	-4.61×10^{-21}	1.72×10^{-15}	-1.85×10^{-10}	8.16×10^{-06}	5.44×10^{-02}
ACE	-1.03×10^{-20}	3.85×10^{-15}	-4.15×10^{-10}	1.83×10^{-05}	1.22×10^{-01}
FLU	-8.17×10^{-22}	3.05×10^{-16}	-3.29×10^{-11}	1.45×10^{-06}	9.65×10^{-03}
PHE	-2.61×10^{-20}	9.76×10^{-15}	-1.05×10^{-09}	4.62×10^{-05}	3.08×10^{-01}
ANT	-3.47×10^{-21}	1.30×10^{-15}	-1.40×10^{-10}	6.15×10^{-06}	4.10×10^{-02}
FLA	-1.86×10^{-21}	6.95×10^{-16}	-7.47×10^{-11}	3.29×10^{-06}	2.19×10^{-02}
PYR	-2.89×10^{-22}	1.08×10^{-16}	-1.16×10^{-11}	5.13×10^{-07}	3.42×10^{-03}
BAA	-2.70×10^{-21}	1.01×10^{-15}	-1.09×10^{-10}	4.79×10^{-06}	3.19×10^{-02}
CHR	-1.11×10^{-22}	4.16×10^{-17}	-4.47×10^{-12}	1.97×10^{-07}	1.31×10^{-03}
BBF	-3.97×10^{-22}	1.48×10^{-16}	-1.60×10^{-11}	7.03×10^{-07}	4.69×10^{-03}
BKF	-3.35×10^{-23}	1.25×10^{-17}	-1.35×10^{-12}	5.94×10^{-08}	3.96×10^{-04}
BAP	-8.95×10^{-22}	3.34×10^{-16}	-3.60×10^{-11}	1.59×10^{-06}	1.06×10^{-02}
IcdP	-3.71×10^{-23}	1.39×10^{-17}	-1.49×10^{-12}	6.57×10^{-08}	4.38×10^{-04}
DBA	-1.07×10^{-21}	3.99×10^{-16}	-4.29×10^{-11}	1.89×10^{-06}	1.26×10^{-02}
BghiP	-3.53×10^{-23}	1.32×10^{-17}	-1.42×10^{-12}	6.25×10^{-08}	4.17×10^{-04}

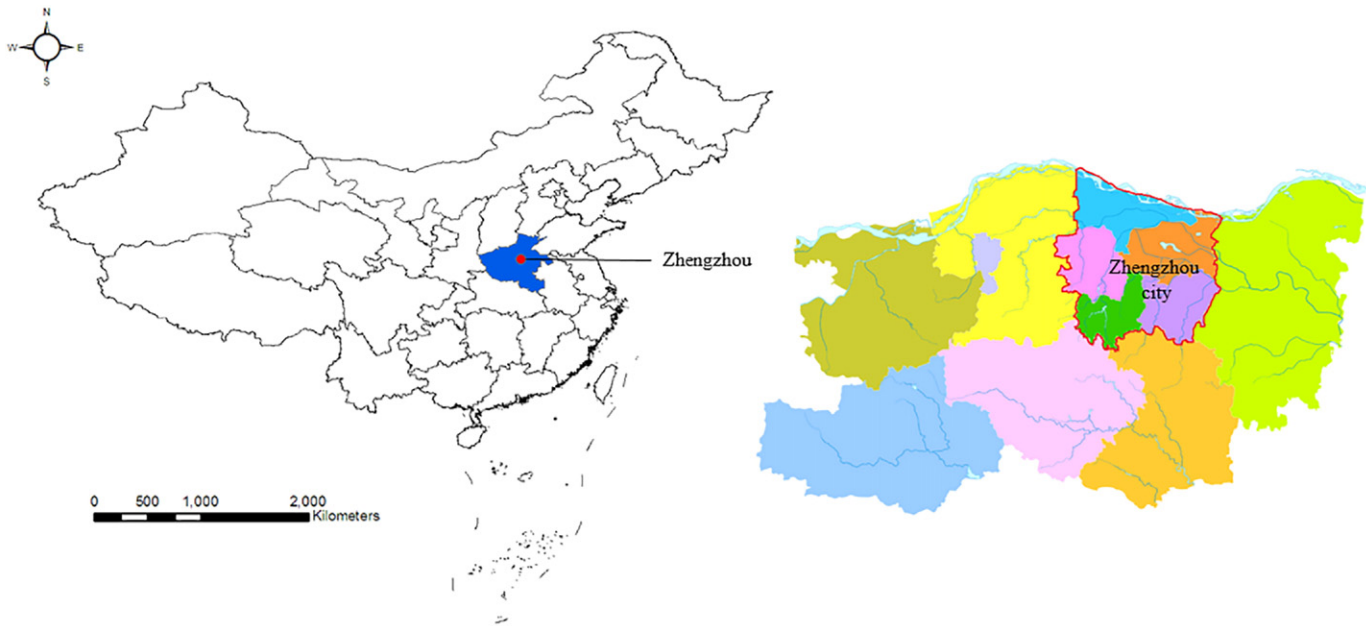

Fig. 2. Location of the study area – Zhengzhou urban area.

methods. Table S3 shows the updated parameters for each VEPAHs and the calibrated Level III model predicted air phase VEPAHs concentrations are much closer to the SAC (in Table S4). Then the updated input parameters were used in the following study. Due to the lack of measured VEPAHs concentration in other compartments, it failed to calibrate other parameters in the multimedia fugacity model.

3.2. Level III model and human health risks

To estimate total concentrations of the sixteen VEPAHs in each compartment, total BaP equivalent concentration was calculated, namely summing the BaP equivalent (BaP_{eq}) concentrations of sixteen VEPAH, and the BaP_{eq} concentration was calculated as a product of VEPAH concentration and correlated toxic equivalency factor (TEF) (see Table S9 in

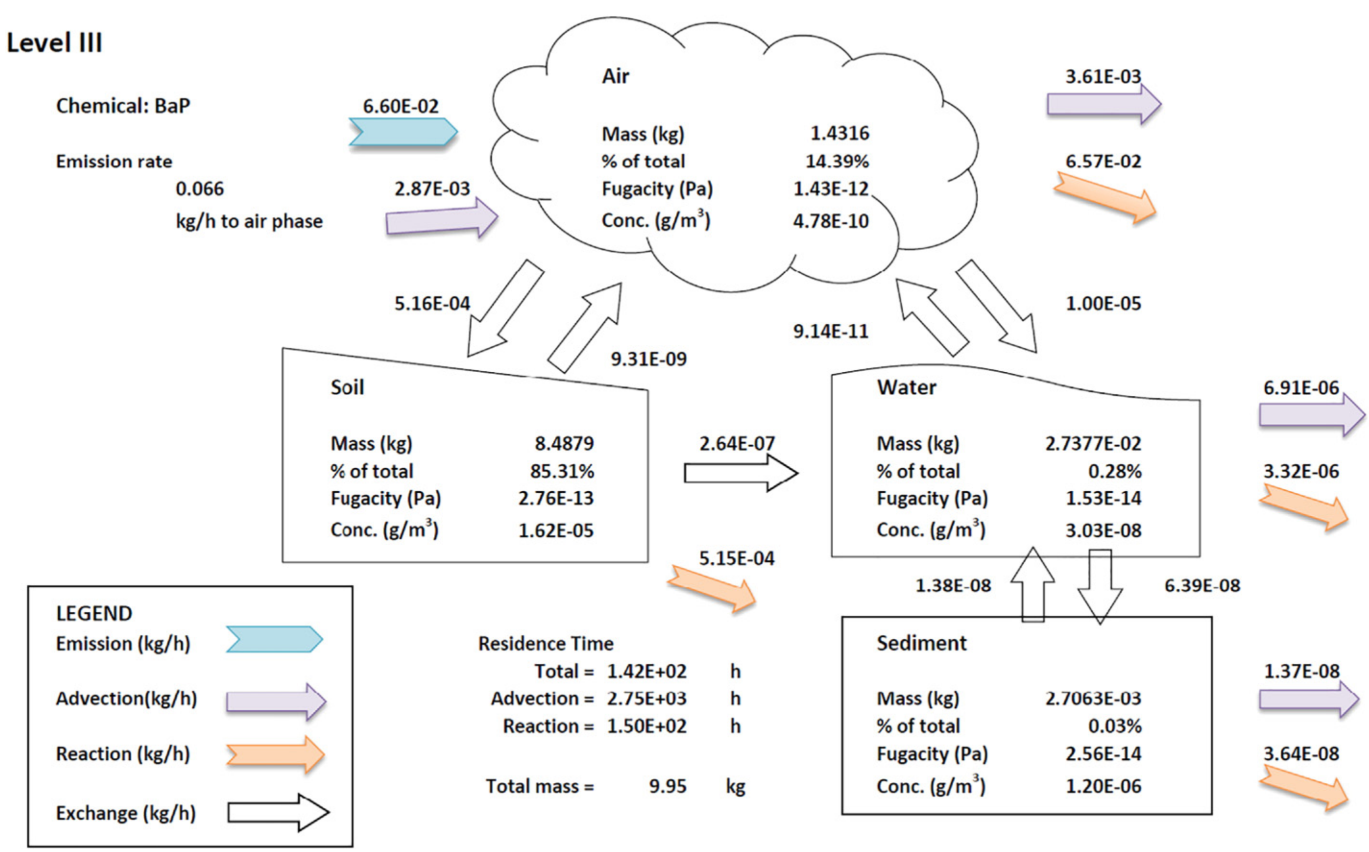

Fig. 3. A schematic representation of multimedia fugacity Level III model results. Steady state mass balance diagram of BAP in air, water, soil and sediment.

the SI) (Yang et al., 2014). As shown in SI Fig. S3, the bar graph depicts total BaP_{eq} concentrations in each compartment, and the major fraction was observed in soil compartment. Since PAHs are lipid-soluble and absorbed into organic carbon, the compounds are easily accumulated in soil organic matters. The pie charts for each compartment show the proportions of VEPAH based on the number of rings to total amount of chemicals analyzed in this study. Noting that light VEPAHs (2 or 3 rings) were dominant in the atmosphere, water, and sediment phases, at the same time, heavy VEPAHs (4–6 rings) are in large amount in soil phases. Due to poorer water solubility and volatility, the heavy VEPAHs preferred to be stored in soil and sediment rather than in air and water.

A schematic representation of the Level III model shows the steady-state mass balance of BaP, which explained the fate and transport processes of target compounds in each medium (Fig. 3). BaP is selected as a representative chemical of VEPAHs and analyzed using the Level III model. The figure shows that most of the BaP in this system would be biodegraded by chemical reactions in the air and then distributed into the air and water compartments by advection processes. Considering 87% SAC as the background VEPAHs concentration, the total input rate of BaP in this study area was 0.689 kg/h. After the chemical entered the ambient atmosphere, 94.1% of airborne BaP was degraded via biological and chemical reactions, and 5.17% was transferred via advection processes. Through intermedia transport process, 0.74% of BaP was deposited into soil and 0.01% was deposited into water. The BaP in water was majorly sourced from atmospheric deposition, accounting for 97.3% of total. In the water phase, 32.3% of BaP was removed by reaction and 67.1% was outputted via advection. In the soil phase, the major part of the BaP was removed by a biodegradation reaction, and the minor of BaP was outputted by advection before migrating to the water phase. The only route of BaP in sediment was deposition of suspended solids in water. The main removal process of sedimentary BaP was chemical reactions (57%), while 21.4% of BaP was reduced by advection process, and 21.6% of BaP in the sediment was re-suspended back to water. The remaining BaP is mainly stored in soil (85.31%) and partially in air (14.39%), and the estimated concentrations of BaP which was accumulated in soil and sediment compartments were 1.65×10^{-5} g/m^3 and 1.20×10^{-6} g/m^3, respectively.

Fig. 4 shows the ILCR results of total and individual VEPAHs to humans. In this study, DBA is considered as the most toxic pollutant among the sixteen VEPAHs. It has an ILCR value of 6×10^{-7}, which represents 46.6% of the total cancer risk to humans. Alternatively, although ACE, and PHE were the two primary VEPAHs with the highest fugacity in the environment, the cancer risks of these two chemicals were at a low level among these VEPAHs. Noting that the concentration of VEPAHs ~~is~~ was not the most principal factors that caused the human health risks. Also, although the concentrations of BbF, and BkF were lower than those of Pyr and Flt, the incremental lifetime cancer risks of DBA and BAP were higher than those of ACE, and PHE Furthermore, the cancer risk posed by VEPAHs also depended on exposure routes. The dominant exposure route of VEPAHs to humans was inhalation in this study, representing 81.6% of the total risk, and the following was the dermal contact and ingestion, representing 17.3% and 1.1% of the total lifetime cancer risk, respectively. Because VEPAHs were mainly introduced into humans via inhalation, residents should be careful to avoid VEPAHs since they caused cancer, even though the fraction of VEPAHs was low in the air phase.

3.3. Sensitivity analysis of the Level III fugacity model with the ILCR model

Sensitivity analysis of the Level III fugacity model combined with ILCR model was implemented for vehicle exhaust BaP to quantify the important input parameters that affected the incremental lifetime cancer risk (ILCR). The sensitivity results are shown in SI Fig. S4. The results of the sensitivity analysis indicate that half-life of chemicals in air, octanol/water partition coefficients (K_{ow}), and cancer slope factor were the most primary factors for all of the exposure routes (i.e., dermal, inhalation, and ingestion). In Fig. S4(a), uncertainty of the total risk was primarily controlled by the uncertainties of the half-life in air (0.84) and cancer slope factor (0.46). For the evaluated cancer risk, the half-life of BaP in air was also a key factor for all of the different exposure routes; these values were 0.76 through dermal contact (Fig. S4(b)), 0.68 through inhalation (Fig. S4(c)), and 0.81 through ingestion (Fig. S4(d)). The sensitivity values of the cancer slope factors were also high for the total cancer risk as well as for the three individual exposure routes. However, their sensitivity values are different for the various routes because the different exposure pathways result in different cancer risks; these values are 0.53 for dermal contact-related risks (Fig. S4(b)), 0.47 for inhalation-related risks (Fig. S4(c)), and 0.56 for ingestion-related risks (Fig. S4(d)). Therefore, the VEPAHs with longer air phase half-lives, lower log K_{ow}, and greater cancer slope factors had the greater influence on human health (in terms of cancer risks). It is important to estimate their detailed effects on human health.

3.4. Prediction of future health risks of residents (Level IV model)

The Level IV model was developed to predict the future health risks of residents when the background concentration was ignored and the

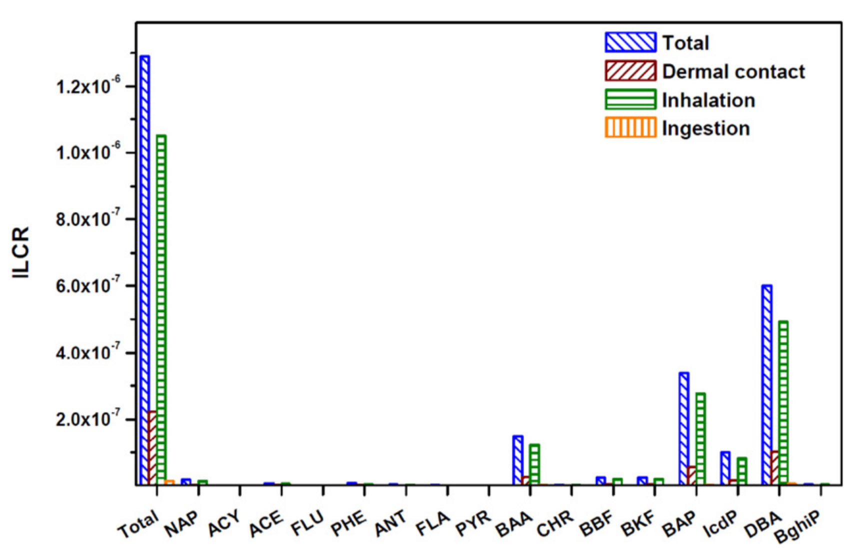

Fig. 4. Total and individual lifetime cancer risks to human caused by sixteen VEPAHs through various exposure routes of dermal contact, inhalation and ingestion.

initial concentration was zero. Because the Level IV model is suitable to a continuous process, the historical VEPAH concentration data were accumulated by year with the trends of the VEPAH emission rates over time. The yearly VEPAH emission rates were calculated by Eq. (S1) using the motor vehicle population data sheet (Tables S5 and S6 in the SI). Then, the emission rates were estimated by a fourth-order polynomial function with the regression parameters listed in Table 1.

The total BaP_{eq} concentrations of VEPAHs were increasing with local vehicle population in the last 17 years, as shown in SI Fig. S5(a). Based on the principle of dissolution in a similar material structure, VEPAHs were accumulated in soil and sediment compartments due to high organic carbon contents rather than in the air and water phases. Therefore, the high VEPAH fraction at the top layer of the sediment and in the vicinity of soil match the conclusion in Level III fugacity model. According to China Ambient Air Quality Standards (GB3095-2012), the year average limit concentration of net BaP is 1 ng/m^3. In air compartment, the highest total BaP_{eq} concentration for the past 17 years was already exceed the net BaP standard limit in 2006 and the tendency was increasing to 2.96 ng/m^3 at the end of 2015. Thus, it was dangerous for the residents of Zhengzhou city to live under these conditions. Therefore, it is necessary to control vehicle exhaust in order to protect the local residents' health.

The incremental lifetime cancer risk (ILCR) was developed to assess the likely cancer risk posed by VEPAHs through the exposure routes of dermal contact, inhalation, and ingestion (Fig. S5(b)). The ILCR evaluation can be assessed against three levels of concern (i.e., no risk, latent risk, and confirmed risk), which are defined by the USEPA (1992). A value of 10^{-4} from the ILCR method indicates the upper threshold, above which serious health issues are expected. The lower threshold is 10^{-6}; below this value, the cancer risk is negligible. ILCR values that fall between the upper and lower limits indicate that people have a potential risk of developing cancer. The highest ILCR value is 2.83×10^{-6} in 2015 (SI Fig. S5(b)), and since 2007 it was beyond the lower limit. It is worthy to note that the estimated ILCR values were the average levels for the whole city and failed to reflect the ILCR for specific types of people such as traffic police, sanitation men, children, or the elderly. The ILCR values of these special cases were likely to be much higher than those of ordinary residents because of the higher exposure level due to longer exposure periods to VEPAHs or to increased personal susceptibility. The future health risks of residents were also predicted by the ILCR model. Fig. 5 shows these estimates in the next 10 years (2016–2025). This prediction was developed using the damped trend non-seasonal method of Crystal Ball. The red dash line implies the fitted and forecast ILCR values, which shows an increasing trend in the next ten years, and the value would exceed the lower limit, indicating that the VEPAHs emission rate would significantly increase the potential risk of causing cancer. The increase in predicted VEPAH concentrations suggests that vehicle emissions should be controlled in the security scope of human via restricting the increase of vehicle population and installing automobile exhaust purifier.

3.5. Health effects of increased VEPAHs in the air phase

The ILCR of inhalation-related VEPAHs was a main factor that caused cancer, as shown above. Therefore, the regression model between VEPAH concentration in the air phase and the mortality rate (respiratory diseases and lung cancer) was established to illustrate their important relationship.

Table S12 in the SI lists respiratory diseases and lung cancer mortality rates during 1999–2015, and reflects the number of people who have died of respiratory diseases or lung cancer per 100,000 residents. The respiratory disease mortality rate data were reported from Zhengzhou city (the capital of Henan province), and the lung cancer mortality rate data were estimated from literatures (Ma et al., 2013; Wang, 2012; Q. Wang et al., 2016; Y. Wang et al., 2016; Y.H. Wang et al., 2016); this provided information of relationship between VEPAH concentrations and potential health effects on humans in Zhengzhou city. Fig. S6 shows the mortality rate as a function of time with the total BaP_{eq} concentration of VEPAHs. The mortality rate of local residents fluctuated over the last 17 years but showed a general increasing trend. It should be noted that the increasing mortality rate of local residents due to respiratory diseases or lung cancer is related to the aging population in China; however, urban industrialization and environmental pollution also have large and crucial influences on the rates of respiratory diseases and lung cancer.

In the regression model, the total BaP_{eq} concentrations of VEPAHs in the air phase were selected as an independent variable. The regression model was established to assess the relationship between the rates of

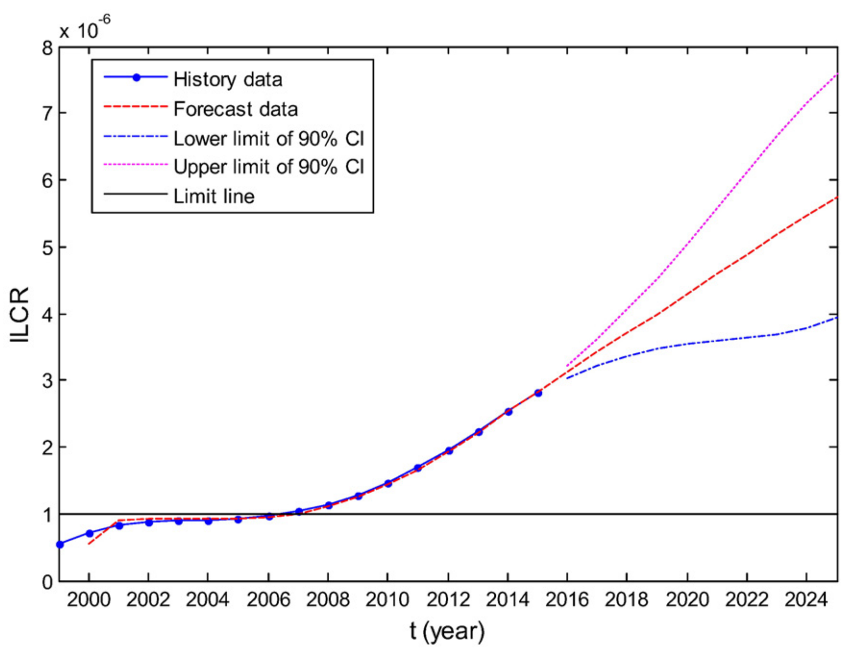

Fig. 5. Total lifetime cancer caused ILCR results of local residences in Zhengzhou during last 17 years from 1999 to 2015 and the prediction of the future 10 years based on the history ILCR.

respiratory diseases and lung cancer and the concentrations of VEPAHs in the air phase, with the R^2 was 0.54 and 0.81, respectively.

$$MR_{respiratory} = 70.39 \times C_{a,total} / (0.95 + C_{a,total}) \quad (1)$$

$$MR_{lung} = 27.04 \times C_{a,total} / (0.22 + C_{a,total}) \quad (2)$$

where $MR_{respiratory}$ and MR_{lung} are the mortality rates of respiratory diseases and lung cancer, respectively, and $C_{a,total}$ is the total concentration of VEPAHs in the air phase. Based on the regression models, the future mortality rates are predicted with the estimated VEPAH concentrations.

Fig. 6 shows the correlation between concentration of VEPAHs in air phase and mortality rates due to respiratory diseases (Fig. 6(a)) and lung cancer (Fig. 6(b)). The mortality rate of respiratory diseases was increasing in the VEPAH concentrations. The observed respiratory diseases death rates from 2000 to 2014 are shown in SI Table S12 and Fig. S6, and the death rate increased at a factor of 2 in this period. The predicted respiratory death rates from 2015 to 2025 indicate that the number of people dying of respiratory diseases will increase to 62 per 100,000 people in 2025. Moreover, Fig. 6(b) shows the lung cancer risks estimated from 1999 to 2014 as well as the predicted lung cancer death rates from 2010 to 2025. The predicted death rate of lung cancer in 2025 is increased 1.3 time compared with the death rate in 1999. Overall, the death rate caused by inhalation-related problems increased as the concentration of VEPAHs in the air phase increased. The increase in death rate in the future, which is shown by this prediction, indicates that environmental monitoring and management are critical, and more substantive policies and actions are required.

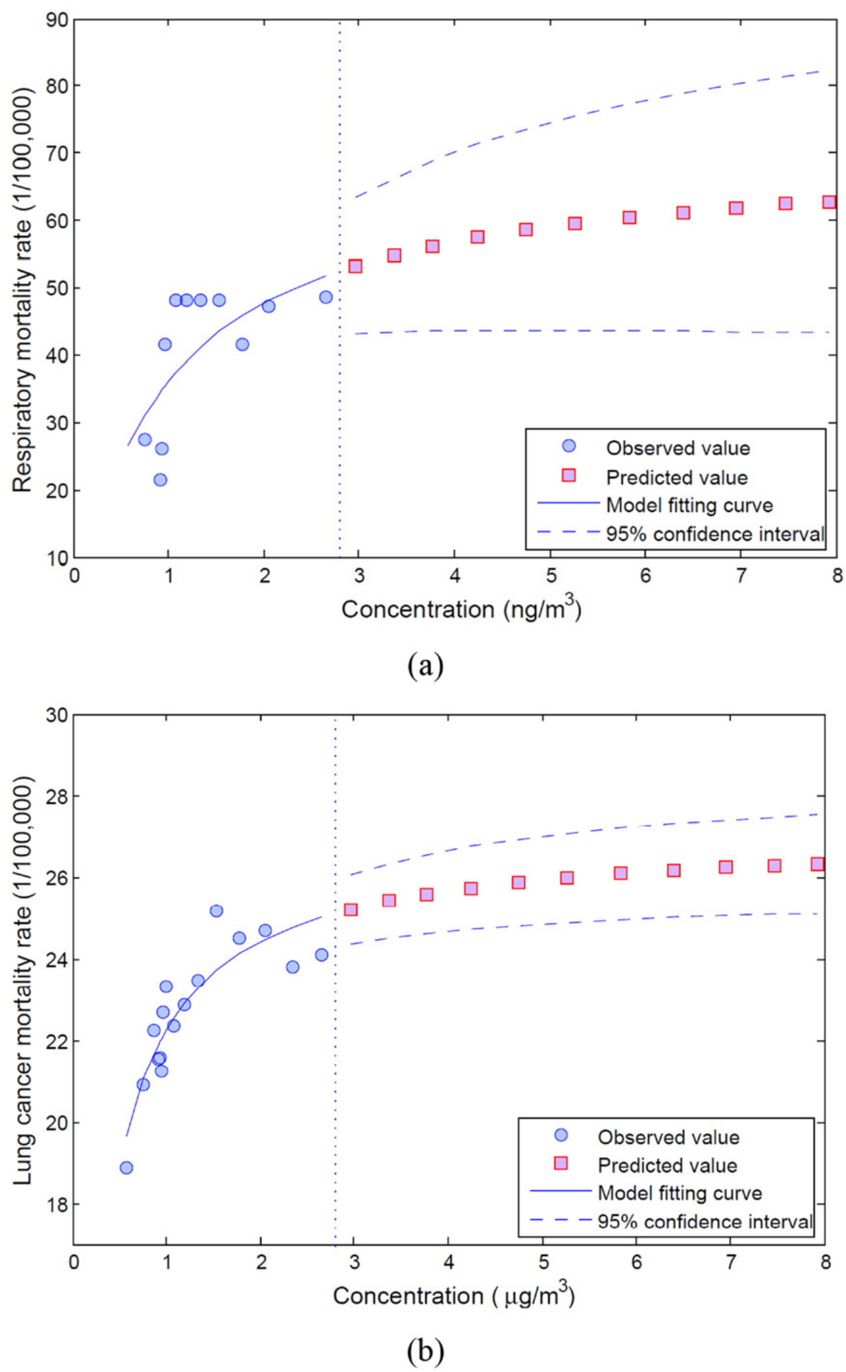

Fig. 6. The relation between the respiratory diseases mortality rate (a), lung cancer mortality rate (b) with the air phase VEPAHs concentration.

4. Conclusions

The multimedia fugacity models (Level III and level IV models) and incremental life-time cancer risk (ILCR) model were implement to find the relationship between the vehicle population and human cancer risk of residence in Zhengzhou. The VEPAHs are high in soil compartment. The multiple pathways of exposure (dermal contact, inhalation, and ingestion) and multiple sources (air, water, soil, and food) of the ILCR model indicate that the cancer risks of VEPAHs follow the order of inhalation > dermal contact > ingestion. The Monte Carlo results confirmed that the emission rate of BaP was the most influential factor on the health risks of these VEPAHs, and the half-life in air, partition coefficient, and cancer slope factor are the main factors that influence the ILCR of BaP. The dynamic ILCR model showed that the increased vehicle population between 1999 and 2015 exacerbated the cancer risks caused by VEPAHs. This study confirms that more attention should be paid to vehicle exhaust PAHs and efficient management strategies should be developed to decrease the lifetime cancer risks of residents in developing cities such as Zhengzhou.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2017.11.084.

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