Multiple Land-Use Fugacity Model to Assess the Environmental Fate of PAHs – A Mega-City Under COVID-19 Pandemic

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Multiple land-use fugacity model to assess the environmental fate of PAHs

– A mega-city under COVID-19 pandemic

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ABSTRACT

Along with the accelerated process of urbanization, the contradiction between social development and environment become increasingly conspicuous. Herein, we access the transport and fate of polycyclic aromatic hydrocarbons (PAHs) by a newly proposed multiple land-use fugacity (MLUF) model to provide comprehensive understanding of PAHs distribution in an urban and suburban areas. PAHs behave differently towards distinct soil types and land covers within the soil phase. We suggest and implement the MLUF model to estimate the PAHs distribution in diverse land types. Moreover, we introduce a multivariate interpretation and systematic model calibration framework to validate the MLUF model adaptability in different land-use area. Accordingly, the organic film on impervious surfaces holds the highest PAHs concentration than other compartments, also soil and sediment phases keep most of PAHs. The potential cancer risk of PAHs in different land-use compartments follow the order of urban green space > agricultural area > forest and semi-nature area. Besides, the dynamic MLUF model is developed and implemented to the period of COVID-19 pandemic for quantitatively estimating the dynamic variations of the PAHs concentration. Finally, we can realize the better scientific understanding of the typical PAHs environmental pollutants transfer phenomena and distribution fates in urban and suburban areas.

Introduction

The industrial revolution has brought rapid development of the economy and improved human living standards; on the other hand, social modernization has also generated severe environmental pollution issues ¹. Currently, many human-made pollutants have exceeded an environment's accommodating ability, and environmental contamination becomes a severe concern for both humans and the overall ecosystem ². To promote the regulation of pollutants releasing and managements through the force of social laws and policies, the environmental fate models that can simulate and predict pollutants behaviour in the environment are getting essential for precise actions ³. Significantly, chemical fate modelling is an effective way to minimize the processing time, cost, and human resources of pollutants chemicals distribution measurements ⁴.

The fugacity-based multimedia modelling is competent in accessing the relationship among organic pollutants physicochemical properties, environmental properties, and the chemical distribution of hazard pollution species in the environment ⁵. Furthermore, the process complexity of the fugacity model can be adjusted regarding the various demands for providing versatile adaptability. The multimedia fugacity (MF) model is a mature technology in predicting organic chemicals' environmental behavior and fate at the global, national, and regional scales ^{4,6}. In some studies of urban systems, chemical fate models are extended beyond the typical MF model to accommodate pollutants transportation in particular environmental condition. Such as the organic films, which stand for the organic coated stationary film on a city's impervious surface area, can be considered a separate compartment ^{7,8}. Also, Song et al. ⁹ designed a Berkeley-Trent-Urban-Rural fate model to simulate the environmental behaviour of persistent organic pollutants (POPs) by treating the air and soil compartments in urban and rural areas independently while considering the advection process in two

compartments' air phase. The air and water compartments have an advective process which induces the uniform distribution of pollutants.

Most organic pollutants are naturally lipophilic, easily dissolved in organic-rich soil compartments. Due to the much longer degradation time of organic pollutants in the soil phase rather than in air and water phases, pollutant concentrations can accumulate and hold significant differences among various type of soil phase¹⁰. The degradation of organic pollutants in soils are initiated by various biotic or abiotic processes, influenced by several relevant factors (like the particular environmental circumstance, unique soil properties, biota, or microbial activities)¹¹. The time required for organic compounds degradation in the environment is enormously differ from place to place. Moreover, most researchers are roughly applying a province or city as a study area when predicting chemical distribution in a real system. It's inadequate to make any straightforward simplification of an environmental phase into a single compartment¹². The different land uses and land covers are the main factors which determine the soil properties in pollutants degradation by interrupting chemicals transport processes, such as volatilization, leaching, and erosion. However, the essential transporting variations among distinct soils are not adopted in the typical MF model. To develop more efficient MF models, the versatile modeling systems construction for chemical fates assessment of pollutants is necessary.

The MF model has essential role in chemical environmental fate understanding. Meanwhile, it's challenging to conduct chemical's environmental behaviors analysis due to the difficulties in accurately collecting realistic model input parameters, such as the chemical emission rate, compartment dimensions, and transport velocities. Minimizing the difference between the calculated concentration and the actual measured concentration of a pollutant is the judgment criterion for the validity of a MF

76 model. A model calibration process is required to be built for estimating the
77 performance of the multimedia fugacity model¹³. And the regularization or correction
78 techniques are typically needed in the MF modelling to guarantee the solution
79 uniqueness and stability of the models¹⁴. A statistical approach is worthy to apply in
80 MF model for performance calibration. However, only a few studies reported the
81 parameter calibration for an MF model before implementing models in a particular
82 place. The chemical environmental fate modelling is particularly sensitive to
83 environmental parameters^{15,16}. We also develop the model parameters calibrating
84 process to realize decent MF models which are appropriate to the specific research area.

85 Herein, we propose a unique multiple land-use fugacity (MLUF) model which
86 consider realistic multiple land-cover types to assess the environmental fate of organic
87 pollutants. The MLFU model provide an efficient way to analysis the organic chemicals
88 behaviors in the environment. In this research, a case study of polycyclic aromatic
89 hydrocarbons (PAHs) distribution in the core districts and Tongzhou district, Beijing is
90 investigate to verify the model performance in differentiate the diverse landcover soil
91 phase behaviour, as the scheme illustration shown in Figure 1. Also, based on the
92 sudden event in the world context, we conduct the dynamic MLUF model on quantitive
93 estimate of the PAHs concentration variation under the impact of the COVID-19
94 pandemic. To validate and calibrate the suggested MLUF model, a multivariate
95 statistical and system analysis framework is constructed for boosting the modelling
96 prediction validity and efficiency. We reduce the data dimensionality through principal
97 component analysis (PCA) and partial least squares (PLS) for visualizing and
98 interpreting the relationships among variables. Finally, the humans and ecosystems
99 risks posed by PAHs to are given in the study area.

100

Results

PAH emission inventory in Beijing. The emission inventory of PAHs in Beijing was investigated and recorded for 18 years, from 2000 to 2017, and the variation in total PAH emissions into the atmosphere is shown in Supplementary Figure S2 (a). The discharge of PAHs tended to increase during the first 18-year of 21 centuries. PAHs' emission was 427 t/year in 2000 with the domain emission source from transport petroleum combustion and followed by domestic coal combustion, coke production, and straw burning. The emissions in 2002 were the lowest amount recorded during the period, 369 t/year. After that, PAH emissions fluctuated with a general rise trend until 2014. The fraction attributed to each emission source is also illustrated in Supplementary Figure S2 (a). Obviously, the structure of PAH emission sources changed dramatically during the study period. There are two point-in-time during the investigated period that met the changes in emission structure. The first one was in 2011, coke production was prohibited in Beijing, and the second time point was in 2015, the straw burning was restricted in the whole Beijing city. Transportation releasing was the dominant source of PAHs in Beijing during the study period, a common phenomenon in megacities. Supplementary Figure S2 (b) shows the contribution of PAHs with different ring numbers to the total PAH emissions in 2010. It is noticeable that PAHs with a low number of rings (2-ring and 3-ring) compose a large fraction of the total PAH emissions, 40% and 35% for PAHs with 2 rings and 3 rings, respectively. PAHs with high molecular weights (4, 5, and 6 rings) make up 25% of all PAH emissions.

In this study, the gross domestic product (GDP) ratio obtained from Beijing Statistic Yearbook between the study area (RMB 92.32 billion) and Beijing city (RMB 141.14 billion) in 2010 was used to estimate the emission inventory of PAHs

due to the potential proportional relationship among GDP and PAHs release ¹⁷. Therefore, the total PAH emission rate in the study area was 33.73 kg/h in 2010 and this emission rate is used to establish the MLUF model and the calibration of this model.

Principle component analysis. Eighty-five parameters of the MLUF model with three different soil compartments were selected and analyzed and these parameters are summarized in Supplementary Table S4. The multivariable results for the output model concentration and the input model parameters implemented by PCA were used to interpret the relationships between those two groups of variables. Characteristics grouped all the MLUF model parameters to identify interactions with the concentration variable, which included chemical properties, environmental properties, compartment size, and mass transfer coefficients (the detail of each parameter is shown in Supplementary Table S3). A visible representation of the first three principal components is shown in Supplementary Figure S3. And Supplementary Figure S3 (a) shows the relation between chemical properties and concentrations. The PAH concentrations in air and vegetation are close to each other and give highly positive contributions to the first principle component (PC1). On the negative side of PC1, logK_{oa} and the concentration in the organic film have considerably high values, which indicates that logK_{oa} (as a thermodynamic descriptor between the air and organic phases) positively affects C_F and negatively influences C_A. Also, C_V shows the same tendency with logK_{oa} as C_A because the respiration of plants makes a large connection between C_V and C_A. The concentrations in soil, sediment, and water are the main factors contributing to the second principal component (PC2) and can be treated as a solubility factor. Meanwhile, logK_{oc} and logK_{ow} make larger contributions to the

soil and sediment factors than the other model parameters. Additionally, the half-life degradation time has a high correlation with a concentration in the corresponding phases. Supplementary Figure S3 (c) shows the relationship between compartment sizes and concentrations. It clearly shows the negative association between concentration and the corresponding compartment sizes. The points of concentration in air and organic film are in the opposite direction with the leaf area index because the absorption effect of plants causes BaP to attach to leaves, which reduces the concentration of PAHs in the air and organic film.

Key parameters selection via PLS-VIP. The environmental characteristics of the various parts of the study area work in synergy with the inherent physical and chemical properties of the PAHs to influence their distribution and ultimate environmental transport and fate. Supplementary Figure S4 illustrates the V-plot obtained by implementing the MLUF model on BaP. The V-plot presents the PLS-derived VIP scores versus the correlation coefficient value for all model parameters. It should be pointed out that correlation coefficients have an obvious disadvantage: the degree to which they approach 1 is related to the number of data sets (n). When n is small, the correlation coefficient fluctuates greatly, and the absolute value of the correlation coefficient for some samples easily approaches to 1; when n is large, the absolute value of the correlation coefficient tends to be small. Therefore, it is inappropriate to judge that variables x and y have a close linear relationship based only on a large correlation coefficient between them. The VIP values show the influence of each model parameter on the model output, and any parameter with a score greater than 1 is generally considered to be important. In the present analysis, the correlation coefficient quantifies the degree of linear correlation

between the model parameters and the model output (concentrations). The emission rate (E_a) has a larger positive correlation with the model output than with the other parameters. The half-life degradation in the air (hf_a) keeps the second-largest effect on the model concentrations. It is evident that the hf_a reflects the decomposition rate of BaP in air, and the air is the only phase with BaP emissions; therefore, to a certain extent, the hf_a determines the quantity of BaP that remains in the air for potential transport to other phases. As shown in Supplementary Figure S4, besides E_a and hf_a , parameters related to the partition coefficient ($\log K_{oa}$, $\log K_{ow}$, and $\log K_{oc}$) and the half-life degradation times in soil and sediment also relative highly influenced the model output on BaP.

The VIP scores of each PAH are summarized in Figure 4. The model parameters with VIP scores lower than 1 are shown in dark blue indicated that these parameters have a minor influence on the simulated concentrations. E_a (parameter 16) and Q_{ain} (or Q_{aout} , parameter 82, 83) had the largest VIP value among the model parameters for all 16 PAHs. As illustrated above, the 85 model parameters were defined in four groups: chemical parameters (parameter 1 to 15), environmental parameters (parameter 16 to 35), compartment sizes (parameter 36 to 48), and mass transfer coefficients (parameter 49 to 85). The chemical parameters show larger VIP values than the other parameters. The partition coefficients ($\log K_{ow}$, $\log K_{oa}$, $\log K_{oc}$, corresponding to parameter 3, 4, and 5) parameters are influential for the model output of all PAHs. Those parameters are related to the partitioning behaviors of the pollutants, a relative indicator of the tendency of an organic compound in one phase to adsorb to another. E_a and hf_a show a high VIP score of all pollutants which is due to the emission sources of PAHs is mostly released into air phase. And the hf_a governs the amount of pollutants transport to the other phases to a large extent. Due to the

sluggishness property of soil and sediment, these compartments are like the universal sink of pollutants and the pollutants can easily accumulate. The degradation is an important process to remove pollutants in soil and sediments, therefore, the hf_s and hf_{se} have relatively high VIP scores in the MLUF model. To sum up, the model parameters of $\log K_{ow}$, $\log K_{oa}$, $\log K_{oc}$, hf_a , hf_s of three land-use soil, and hf_{se} , h_a , were selected as the input variables for the GA to calibrate the model concentrations to the study area.

Estimated environmental fate of PAHs via MLUF model. The calibrated concentrations were compared with observed PAH concentrations to verify the model performance. The total PAH concentration and PAH equivalent concentrations are illustrated in Supplementary Figure S5 (a) and (b), respectively. The PAH equivalent concentration was derived by considering the toxicity of each chemical and multiplying the concentration of each PAH by a toxicity equivalence factor (TEF). The simulated (bar plot) and observed concentrations (the maximum, mean, and minimum values are shown as red points) were compared in each environmental compartment, air (ng/m^3), water (ng/L), soil (ng/g), sediment (ng/g), vegetation (ng/g), and organic film (ng/m^2). The model-estimated total PAH concentrations and the equivalent PAHs concentration are consistent with the measurements (within the lower and upper boundaries of the reference concentrations). Therefore, the proposed MLUF model can be conducted to predict the environmental fate of PAHs. The calibrated parameters were also implemented in a typical MF model (single soil compartment) to compare the results with those from multiple soil compartments. The calculated PAH concentrations (in 2010, same year base with MLUF) of MF model which consider soil as single compartment at the study area is shown in

Supplementary Figure S6, and the results show that the calibrated parameters are suitable for estimating the PAH distribution in the study area. The estimated total PAH concentrations in the MF model and the proposed MLUF model are compared in Supplementary Table S11. Because the environmental compartments in these two models varied, the estimated concentrations vary slightly in each compartment. The PAH concentrations calculated by the MLUF model in the soil compartments and vegetation under different land uses shown the highest value in city gardens and the lowest value in the FSNA. The single-compartment (soil or vegetation) PAH concentrations are in the same range as the multiple-compartment PAH concentrations. Among the evaluated PAH concentrations, the PAH component patterns differed among each compartment (Supplementary Figure S7 (a)). The low molecular weight (LMW, less than four benzene rings) PAHs appear abundantly in the air and water phases because of their relatively high vapor pressure and water solubility. In other compartments (soils, sediment, vegetation, and organic film), high molecular weight (HMW, more than three benzene rings) PAHs are predominant because they partition more readily into organic matter. PAHs with a large TEF value contribute more than other PAHs to the PAH_{seq} concentration (Supplementary Figure S7 (b)).

In the study area, 295.45 tons of PAHs were released into the air compartment in 2010 and distributed to other compartments through portioning and transport processes. An equilibrium state can realize according to the theories in the steady-state fugacity model. The mass balance diagram of the $\sum_{16}PAHs$ fate and transport processes is shown in Figure 5, with a total $\sum_{16}PAH$ emission rate in the atmosphere of 33.73 kg/h. Once PAHs have been released into the ambient atmosphere, most of them are transport through advection (121.39 kg/h). Due to the short half-life

degradation time in air, 31.8 kg/h PAHs were removed from air compartment through degradation. The 5.72% portion PAHs in air phase transports to other compartments. Among those remaining PAHs, HMW PAHs tend to behave like solid particles in the atmosphere. Due to the adsorption of particulate matter by plants, most of the air phase remaining PAHs were deposited into vegetation (with 4.36, 8.38, and 1.56 kg/h for agriculture, FSNA, and urban green space, respectively). Only 0.21% of PAHs dissolve in the water compartment. Meanwhile, 82.28% of PAHs were removed by the reactions, and 5.94% were transferred to other cities through the air. At equilibrium, most released PAH pollutants in air are removed by responses in the other four compartments, consisting of 93.77% of all the discharged PAHs in the study area. The remaining 7.23% of PAH pollutants were found enriched in the soil phase. In other words, the soil phase holds 95.69% of all remaining PAHs in environments. When considering the volume of the phases, the PAHs concentration in the organic film ($6.19 \times 10^3 \text{ mg/m}^3$) is highest, and the second-highest case is the city green space soil-type phase ($3.90 \times 10^3 \text{ mg/m}^3$).

The effect of land-use changes on the environmental fate of PAHs. The calibrated MLUF model was implemented to predict the PAH distributions in 2015 and 2020 by projecting the various emission rates and land-use areas within the overall study area. In this study, the PAH emissions in 2020 regards the same as 2015 by considering the city development has slowed down and the PAHs emission source structure tending towards the stable. The land-use areas between 2015 and 2020 have changed according to municipal planning with keeping the area of urban construction land and improving the ecological land use. The land-use (agriculture, city green area, water area) of the study area in 2020 is estimated via the linear regression model based on the general plan for land use and land-use changes in Beijing from 2012 to 2017, in which the land-use data

from the Beijing statistical yearbooks (as shown in Supplementary Figure S8). The modelled multicompartment Σ_{16} PAHs concentrations show higher value in 2010 compared with 2015 and 2020 (except water and sediment compartments) (Table S12). Compared to the land-use change between 2015 and 2020, the areas of farmland, urban green space, and water are reduced by 4.69%, 8.22%, and 5.04%, respectively. The FSNA area is increased by 8.54% and the urban construction area is increased by 0.62%. The Σ_{16} PAHs concentration in water and sediment compartments shown a rising trend. There are two possible reasons to cause this phenomenon, one is due to the water area is descending and the second is the increase of urban construction area induced more PAHs transfer from organic film to water compartment. In the air, vegetation, and organic film compartments, the Σ_{16} PAHs concentration had slightly increased. The increase of FSNA caused the Σ_{16} PAHs concentration have a 0.02% decrease in FSNA soil. The mass of PAHs in the various environmental compartments depends on the concentrations and compartment sizes. The changes in the land-use area also directly influence the PAHs mass content in each compartment. The PAHs in water, sediment compartments are decreased, on the contrary show increasing in air and organic film compartments. The land-use changes in soil compartments lead to similar changes happened in the soil and vegetation compartments. The soil compartments area changed by -4.69%, 8.53%, and -8.15%, corresponding to agriculture soil, FSNA soil, and city green area. Through this MLUF mode, the pollutants dynamic distribution responses along with the city developments could be performed for subsequently providing scientific guidance and adequate actions to environmental regulation.

Risk assessments. Risk assessments about the environmental PAHs were carried out for both human health and ecological systems under the 2010 case, and the results are

shown in Figure 6, where the red points stand for the total risk posed by the 16 PAHs, and the stacked bar chart shows the contribution of each PAH to the total risk. Figure 6 (a) expresses the human ILCR values retained by PAHs in different areas through various exposure routes. In this study, inhalation was the dominant route of human exposure to PAHs, followed by dermal contact and ingestion. The ILCR values for different land cover regions with different land cover followed the urban green space > agricultural > FSNA, indicating that the urban green space soil is more hazardous than agriculture soil and FSNA soil. The ILCR exposure by 5 rings PAHs occupy more than 85% of the total ILCR through all exposures routes due to the higher health risk pertained by the 5 rings PAHs than the other PAH species. Therefore, the emission rates of the PAHs are not the principal element that influences health risk. Even though the LMW PAHs have the highest emission rates, but their risk just occupies less than 2% of the total ILCR. As a consequence, more attention should be assigned to the fates and distribution of the high ILCR PAHs species in soil from society.

The risk assessment for the ecological systems of water, soil, and sediment estimated hazard values are shown in Figure 6 (b). In the study area, the sediment and water phases have higher ecological risk, with a value of 1.74 and 1.50, respectively, indicating that the PAHs released in the study area pose a hazard to aquatic organisms. The HMW PAHs show more substantial contributions to the RI value in the water phase. The RI in the soil compartments was lower than the limit values, indicating that those PAH concentrations are within the acceptable range in the soil compartment of three land-use. Compared with the RI in the water phase, LMW PAHs accounted for a larger proportion of the risk by PAHs in sediment and soil ecosystems. The RI value for different land covers followed the order of urban green space > agricultural area > FSNA, indicating that the soil in urban green space is more hazardous to the ecological

system than agricultural soil and FSNA soil. The contribution of each PAH to the RI also differs by land cover. In agricultural soil, the HMW PAHs (5 and 6 rings) account for more than 77% of the total PAHs ecological risk, show 66% and 61% in FSNA and urban green space, respectively. The results of this study have significant implications for urban planning and decision making when working to protect and remediate water and habitat quality in Beijing, also the assessment techniques which described here are applicable to other study areas.

The spatial distribution of PAHs caused ILCR is shown in Figure 7. The land use information of the study area is extracted based on the Beijing Land Use Planning (2006 - 2020) and Wanghe et al.¹⁸. Continue PAHs posed healthy risk were predicted by interpolation with the ILCR estimated by MLUF model and health risk model through multiple exposure routes in different land-use using the inverse distance weight method in ArcGIS 10.5. Any substance with an ILCR value higher than 10^{-6} and lower than 10^{-4} is considered to be potentially carcinogenic¹⁹. The study area has been exposed to excessive PAHs and could therefore face high potential health risks. In the study area, people PAHs exposure health risk is higher in the central city area of core districts in Beijing and Tongzhou district. As a new urban development area in Beijing, Tongzhou district is dominated in an agricultural area with 37.6% rather than the 5.2% in core districts. Attributed to the high agricultural area percentage of Tongzhou district than Beijing core districts, the ILCR caused by PAHs in Tongzhou district is lower than the core districts. With the land-use information, the MLUF model integrates with risk model can effectively distinguish the pollutants concentration distribution in soil phases.

The dynamic MLUF model implement on the changes of PAHs concentrations in

the study area during the COVID-19 pandemic. The dynamic MLUF model is implemented for the first four months in 2020, which covered the epidemic outbreak and got under control in Beijing. The emission of PAHs from transport is estimated by the travel intensity index in Beijing, as shown in Supplementary Figure S10²⁰. According to the travel intensity index, a trafficking factor is calculated to reflect the traffic volume reduction due to the restriction and control measures. Four stages are considered according to the dataset. On the first day of 2020, WHO had set up the IMST (Incident Management Support Team) to dealing with the COVID-19 outbreak. Therefore, the early stage is defined as regular travel, which is the period before the Chinese lunar New Year and the time that the majority of people knew nothing about this new coronavirus. As the Lunar New Year approaching, some migrant workers were started to return to their hometown after January 18th, and the inner-city travel intensity index had been steadily reducing, as shown in Supplementary Figure S10, which continued for around one week as considering the second stage. At the end of the second stage, the news of human-to-human transmission of novel coronavirus has been reported and known by the most public. The widespread news of the novel coronavirus coming out leads to a lower inner-city travel intensity index than in the same period of 2019, Supplementary Figure S9 in Supplementary Information (SI). The third stage is home quarantine, which from January 26th to February 9th. In this period, the traffic in Beijing city remains at a low level compared with other years. The fourth stage is a step by step return to work since February 10th. The linear piecewise functions are developed to describe the traffic factor during this period, as shown in Eq. (9).

$$f_{traffic} = \begin{cases} 1, & t \leq 18 \\ -0.11t + 1, & 18 < t \leq 25 \\ 0.23, & 25 < t \leq 40 \\ 0.0056t, & 40 < t \leq 121 \end{cases} \quad (9)$$

where t stands for the day counting start from January 1st to April 30th, and $f_{traffic}$ is the traffic factor. The PAHs released from transportation are calculated by multiply the traffic factor with the estimated transport PAHs emission in 2020. As shown in Supplementary Figure S10, the traffic factor calculated by the simple linear regression can predict the traffic volume trend during the epidemic period.

The dynamic MLUF model estimates the concentration of Σ_{16} PAHs in the first four months of 2020, and the concentration in each compartment are shown in Figure 8. Due to the reduction of emission, the total PAHs concentration is shown a decline during this period. The overall decreasing rate of total PAHs concentration is calculated with the initial level and the concentration at the end of the analysis period summarized in Table S13. PAHs concentration in water phases presents the most significant changes. However, in soil and sediment phases, the Σ_{16} PAHs concentration shows fewer changes, indicating that the PAHs are more stable in these phases than air, water, vegetation, and organic film due to the longer degradation time. During this period, the PAHs emissions go through dramatic decreases to a relatively lower level and rise gradually. However, the Σ_{16} PAHs concentration in soil and sediment phases has a minor reflection of the decline in emission, as shown in Figure 8 (c-f). The predicted concentration is monotonically decreasing in this period. The emission changes show the most considerable influence on the concentration in the air phase. The Σ_{16} PAHs concentration in the air decreased by 51.59% compared with the concentration before the COVID-19 epidemic due to the home quarantine in stages 2 and 3. It gradually increased by 63.61% compared to the lowest concentration along with the step-by-step restoration of the economic activity. Due to the lower degradation time and advection rate compared with the air phase, the Σ_{16} PAHs concentration in water shows slightly smaller change, reducing 48.35% in stages 2 and 3 and increasing 54.75% in stage 4.

For the vegetation and organic film compartments, the Σ_{16} PAHs concentration is sensitive to the variation of emission due to the close relations with the air phase. Considering the land-use in the study area, the vegetation compartment in the city green space is more sensitive to the PAHs emission changes than the other lands. The PAHs concentration in the city soil compartment is more stable than the different land-use with a reduced rate of 2.64%. The concentration reduction rate differs in various land-use indicated that the PAHs pollutants in city soil are hard to remove by natural degradation processes.

Discussion

A steady-state MLUF model was proposed and successfully implemented to transferring dynamics and chemical fate estimation of PAHs pollutants in Beijing, China by considering the soil phase variances to several detailed realistic compartments. The MLUF modelling process was calibrated by multivariate interpretation and systematic model, and reached comprehensive validation. And we selected the essential model parameters of MLUF through the unique approach of PLS-derived VIP scores versus the correlation coefficient values. We acquired the spatial distributions of the 16 kinds of PAHs species in soil phases of the study area from the MLUF model. The PAHs movement and transformation properties inside the compartments were determined for representing the estimated mass transport rates. After performing the risk assessment, we first time obtained the ILCR health risk values in the different land covers that follow the urban green space > agricultural area > FSNA. In terms of ecological risk, the RQ value for different land covers followed the same sequence with ILCR case, indicated the more hazardous risk possessed in urban green space soil than agricultural and FSNA soil. Interestingly, we observed the

obvious concentrations changes quantitatively during the COVID-19 pandemic in the study area through implementing the proposed dynamic MLUF model. The significant influence of the COVID-19 outbreak on PAHs concentration was discovered in the air, water, vegetation, and organic film compartments. This study provides a thoroughly scientific understanding of environmental pollutant transport in urban areas with the most recent environmental and social information and can be applied to facilitate various land conservation and sustainable development efforts.

Methods

Model description. The MLUF model is established based on an MF Level III model to evaluate the pollutant fates in six main compartments, i.e., air, water, soil, sediment, vegetation, and impervious surfaces (organic film), shown in Supplementary Figure S1. The air compartment consist of gas and particulate matter. The water compartment consists of water and particulate matter. The sediment compartment is regarded as a layer of deposited particles at the bottom of the water body. In the urban environment, impervious surfaces, such as buildings and roadways, make up a large proportion of the downtown area, impeding the mass transfer between air and soil compartment. Especially, an organic film coated on the impervious surfaces is considered as a single compartment in the strategy of MLUF model. The absorbed organic pollutants was considered mainly migrates from impervious surfaces to water compartment rather than soil compartment through rain wash-off into urban drainage system. As one of the unique aspect in this report, the soil compartment in MLUF model is splited into several independent sub-compartments to be more realistic and each soil sub-compartment is considered to carry independent transport behaviors of pollutants compounds with other compartments. The separation of soil compartment

is based on the land-cover types. According to different land cover, the vegetation compartment is separate to different sub-compartments. The mass-balance equation in each compartment of the MLUF model assumes that the total input of chemicals is equal to the sum of the total output and the accumulation, as following:

$$E_i + Q_{in} \cdot C_i + \sum (D_{ji} f_j) - f_i (\sum D_{ij} + D_{Adi} + D_{Ri}) = \alpha \quad (1)$$

where E (mol/h) is the emission rate, D (mol/Pa·h) is the transport parameter, f (Pa) is the fugacity of chemicals, C (mol/m³) is the concentration of the pollutant, and Q_{in} (m³/h) is the advection flow rate of air and water. The subscript Ad represents the advective process, R is the reaction, and i and j represent environmental compartment numbers. On the right side of the equation, α interpreted as 0 in the steady-state model and $V_i Z_i \cdot \frac{df}{dt}$ in a dynamic model, respectively. The steady-state mass balance equations of chemicals in each compartment are summarized in Table 1. Subscripts A, W, S, Se, V, and F are defined as air, water, soil, sediment, vegetation, and organic film, respectively. For different soil and vegetation compartments, n is used to distinguish different sub-compartments. The chemicals concentration of each compartment is computed by multiple fugacity capacity with the fugacity. The details of computing fugacity capacities (Z) and transport processes (D) are shown in Tables S1 and S2.

Systematic model calibration framework for MLUF model. Figure 2 illustrates the framework for the systematic model calibration of the MLUF model using a multivariate statistical analysis method. In this study, PCA and PLS were implemented to find the relationships among parameters and select the critical parameters that would allow the proposed model to precisely predict the environmental behavior of organic pollutants. Firstly, the process of predicting the environmental fate of a pollutant chemical was conducted using the proposed MLUF

model. At second, the Monte-Carlo simulation method was applied to the fugacity model with a random combination of model parameters to obtain an experimental data set. Thirdly, auto-scaling was used in data preprocessing to normalize the data. Then, using PCA and PLS, the parameters were grouped, and sensitive variables were investigated. A system analysis of the MLUF model was conducted for the affected variables to identify how those parameters influence the model output. Such a model calibration is required before an MF model can be applied to predict chemical behavior. The PAH concentrations measured in each compartment were gathered from the literature and compared with the concentrations calculated in the model calibration process. In the end, a genetic algorithm (GA) approach was used to optimize the model parameters by minimizing the deviation between the modelled and observed PAH concentrations. The description of systematic model calibration methods are shown in SI, and the MLUF model parameters are listed in Supplementary Table S3 and S4.

Case study

PAHs. As a class of persistent contaminants, PAHs have a relatively long degradation time in the environment, are easily diffused and able to travel a long way in the environment. Especially, PAHs are an increasing concern because they are highly toxic to humans and ecological systems. In this study, 16 priority ordinary PAHs were selected basing on the potential human and ecological health effects according to the claim of U.S. Environmental Protection Agency (USEPA): naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benzo[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF),

benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IcdP), dibenzo[a,h]anthracene (DBA), and benzo[ghi]perylene (BghiP). Their physicochemical properties are summarized in Supplementary Table S5²¹.

PAHs are released into the ambient environment by several natural and anthropogenic processes²². Since the second industrial revolution, PAHs' human-caused emissions have become substantial because of the rapid increase in burned fuel for industrial manufacturing, transportation, and heating applications²³. An elaborate emission inventory needs to be estimated to establish an accurate model for predicting PAHs' environmental behavior. In Beijing, the following PAHs emission sources were identified: (1) industrial coal combustion, including thermoelectric power stations and heating plants; (2) domestic coal combustion, including the residential and commercial sectors; (3) coke production; (4) transport petroleum combustion; (5) other petroleum combustion; (6) straw burning; and (7) cooking. The total emission of PAHs is the accumulation of the emission inventory from each source. The emission inventory (Q) of each chemical from each release source is calculated according to the emission factor (EF) and emission activity (EA), as shown in Eq. (8).

$$Q = EA \times EF \quad (8)$$

The emission factors differ among PAH species and emission sources, and they are listed in Supplementary Table S6. According to these reported data in Supplementary Table S6, it can be observed that the industrial coal combustion process produced less PAH than domestic discharge (domestic coal combustion, straw burning, and cooking) which may attribute to the more adequate combustion process. Straw burning has the most considerable unit-emission rate. Due to China's particular cooking style, the PAHs released during cooking are also considered in this study (Eq. S7). The detailed calculation of PAHs emission inventory from each emission source is shown in SI.

524

525 **Study area.** Beijing is the capital city of China and plays an important role as the
526 country's political, economic, and cultural center. And, Beijing is located in the
527 Northern part of China (116°20' E, 39°56' N) (Figure 3), and it has been experiencing
528 a relative air pollution concern continually. Besides, Beijing typically has a warm,
529 temperate, sub-humid continental monsoon climate, and it is surrounded by the Yan
530 Mountains and Loess Plateau on three sides. Pollution easily becomes trapped and
531 accumulates in this area due to weak atmospheric ventilation ²⁴. The geographical
532 impact, industrialization, and urbanization are the important causes of the pollution in
533 Beijing and its adjacent areas. As the city's environmental problems become a more
534 widespread concern, environmental protection measures have been put forward, and
535 more stricter environmental rules have been enforced during the past decades.

536 The study area consists of six core districts and Tongzhou district of Beijing, which
537 is a typical urban and suburban area. According to the Beijing Municipal Bureau
538 statistics in 2012, 58.7% of the study areas are urban and townland, which is assumed
539 as artificial impervious surfaces in the MLUF model of this study. The remaining areas
540 are agricultural land (18.4%), forest and semi-nature area (FSNA) (13%), and urban
541 green space (3.6%). All those land types comprise the multiple land-use parts of this
542 study. Supplementary Table S8 shows the compartment dimensions of the study area.

543

544 **Risk assessment.** As a group of hazardous POPs, PAHs have potential or identified
545 carcinogenicity and genotoxicity ²⁵. Therefore, it is cardinal significant to implement a
546 thorough toxicity analysis of PAHs. In this study, the incremental lifetime cancer risk
547 (ILCR) is applied to estimate the potential human health risk caused by the 16 PAHs.
548 People exposed to PAHs from the ambient air, water, and soil is mainly through three

exposure routes, including dermal contact, inhalation, and ingestion ²¹. Moreover, the related ecological risk of the PAHs in the study area are also evaluated to present a comprehensive understanding of the pollutants risks. Ecotoxicity endpoint tests, such as LC₅₀ (the concentration of a chemical at which 50% of the test organisms die), LD₅₀ (median lethal dose), and NOEC (no observed effect concentration), are conducted to determine the level of a substance's hazardous effects to the environmental compartments. To assess the ecotoxicity of a chemical, a risk quotient (RQ) is suggested by the USEPA, which is calculated based on the dose of exposure and ecological effects data ²⁶. In this study, the chronic risk is used to estimate the ecological risk posed by PAHs. The estimated concentration of each PAH in the ecosystem (soil, water, and sediment) was divided by its effect toxicity value to derive an RQ, and the risk index (RI) in each compartment for all PAHs is calculated by the sum of the RQ of each PAH. The details of the risk assessment equations are shown in SI. The parameters of the human health risk model and ecological risk model are shown in Supplementary Table S9 and S10.

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Authors' contributions

Q. L.: Conceptualization, Methodology, Validation, Writing original draft. P. V.: Formal analysis. K. N.: Formal analysis. C. Y.: Conceptualization, Supervision, Review & Editing, Funding acquisition.

Competing interests

The author(s) declare no competing interests.

Ethics declarations

This article does not contain any studies involving human, animal, or plants participants performed by any of the authors.

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656

Figure Captions

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Figure 2 | The proposed systematic model calibration method for the multiple land-use model.

Figure 3 | Location of the study area — downtown and the Tong Zhou district area of Beijing.

Figure 4 | The selected model parameter in multiple land-use fugacity model via VIP scores for each PAH.

Figure 5 | Estimated PAH transformation and fate inside the compartments, as determined by the multiple land-use fugacity mode.

Figure 6 | Risk assessment of (a) human and (b) ecological system exposure to PAHs in the study area.

Figure 7 | Spatial distributions of Σ_{16} PAHs caused ILCR of the study area based on multiple land-use fugacity model.

Figure 8 | The dynamic variation of Σ_{16} PAHs concentration during the COVID-19 pandemic in each compartment. (a) air, (b) water, (c) soil_agriculture (d) soil_forest (e) soil_garden (f) sediment, (g) vegetation_agriculture, (h) vegetation_forest, (i) vegetation_garden, and (j) organic film.

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(a)

(b)

(c)

(d)

(e)

(f)

(g)

(h)

(i)

(j)

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720

Table Captions

721 **Table 1** | The mass balance equations for each compartment in MLUF model.

722

Table 1 | The mass balance equations for each compartment in MLUF model.

Compartment	Mass balance equation	Eq.
Air	$E_A + Qin_A C_A + D_{WA} f_W + \sum_{n=1}^p (D_{SnA} f_{Sn} + D_{VnA} f_{Vn}) + D_{FA} f_F$ $= f_A \left(Da_A + Dr_A + D_{AW} + \sum_{i=1}^n (D_{ASn} + D_{AVn}) + D_{AF} \right)$	(2)
Water	$E_W + Qin_W C_W + D_{AW} f_A + \sum_{i=1}^n (D_{SnW} f_{Sn}) + D_{SeW} f_{Se} + D_{FW} f_F$ $= f_W (Da_W + Dr_W + D_{WA} + D_{WSe})$	(3)
Soils	$E_{Sn} + D_{ASn} f_A + D_{VnSn} f_{Vn} = f_{Sn} (Dr_{Sn} + D_{SnA} + D_{SnW})$	(4)
Sediment	$D_{WSe} f_W = f_{Se} (Dr_{Se} + D_{SeW})$	(5)
Vegetation	$D_{AVn} f_A = f_{Vn} (Dr_{Vn} + D_{VnA} + D_{VnSn})$	(6)
Organic film	$D_{AF} f_A = f_F (Dr_F + D_{FA} + D_{FW})$	(7)

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