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Simulation Tool for Assessing the Environmental Distribution of PAHs Contamination

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***Abstract*- Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants. Excessive inputs from anthropogenic activities have caused serious PAHs contamination and adversely affect the health of creature life and human through bioaccumulation. The objective of this study was to investigate fate and transport modeling of Benzo[a]pyrene (BaP) that is commonly used as an indicator species for PAH contamination. Fugacity model level III was developed under steady state assumption to assess the environmental distribution of this substance contamination in Dong Rui mangrove. The results showed that the BaP was existed in majority in soil and sediment compartments and advection process attributed for BaP transference among the environmental compartments.**

Keywords: PAHs; mangrove soil; toxicity assessment; fugacity model.

I. INTRODUCTION

Polycyclic aromatic organic compounds (PAHs) are formed from the molecules H and C and are composed of interconnected benzene rings. They are a ubiquitous group of several hundred chemically related compounds, environmentally persistent with various structures and varied toxicity. They have toxic effects on organisms through various actions[1]. PAHs are formed primarily by incomplete combustion of raw materials and fuels from industrial, movement and living sources. They have the ability to spread far in the environment and accumulate in compartments such as soil, water, air and sediment. Many PAHs are carcinogenicity and germ cell mutagenicity[2]. Dong Rui mangrove forest is a very special area, the downstream area of the rivers and adjacent to the estuary. It is located in Quang Ninh province, Vietnam. It is surrounded by three rivers such as: Ba Che, Voi Lon and Voi Be. This mangrove ecosystem is known as diverse and rich abundant in fauna and flora. It has great impacts on the protection and prevention of storms and floods and brought about great fisheries resources for people, which have been paid special attention by scientists, researchers and authorities. In 2007, Dong Rui mangrove forest was identified as one of 12 most degraded ecosystems.

Very few studies have shown that the presence of PAHs in water and sediment in Cua Luc, Tra Co, and Ha Long Bay [3, 4], especially in Dong Rui mangrove forest. This area is located at Cua Ong where coal mining activities took place hundreds of years with a distance of 200 km in upstream. In the wet season, the discharge from the coal sites enters either to the streams down to Voi Lon and Voi Be Rivers or directly runs to the estuary. Addionally, Dong Rui mangrove forest is far 7 km from Mong Duong 1 and Mong Duong 2 thermal power companies which can be attitude to the PAHs desposition into air. Dong Rui mangrove also has diurnal tidal phenomenon to happen regularly that are considered as PAHs intrusion on the soil and River body through up and down tides. It is likely, Dong Rui mangrove can receive PAHs contaminants from the air and rivers.

Mangrove forest were accumulated PAHs with wide range concentration in 2015, 2016 [5,6]. The findings were reported that average concentration values of total 16 PAHs in Dong Rui mangrove forest (RNM) was at 958.9 ± 488.2 µg/kg. It can be understood that PAHs are hydrophobic and readily adsorbed onto particulate matter, therefore, coastal and marine sediments become the ultimate sinks and elevated concentrations were been recorded [3,4,5,6]. Mangrove ecosystems, important inter-tidal estuarine wetlands along coastlines of tropical regions, are closely tied to human activities and are subject to contamination. The mean concentrations of PAHs in Dong Rui mangrove forest were lower than those in Iran (1585 mg/kg) and Hong Kong (1992 mg/kg), but higher than those in Deep Bay in China [7,8,9].

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Among compounds of PAHs, the concentration of BaP was the highest (82.53 µg/kg), following by Ind (77.72 µg/kg), Flt (74.73 µg/kg), BaA (73.32 µg/kg) and BbF (65.83 µg/kg). These substances are listed as carcinogenicity. Therein BaP is considered as the typical substance for the PAHs. Because, BaP compound was acute toxicity, high bio-accumulation, carcinogenicity and widely spread in the environment [7,10,11].

Different models have been constructed for quantitative simulation of fate of chemicals in the environment [10,11]. Among them, fugacity mode proposed by Mackay (1979) is the most popular model with many successful case studies on the fate of organic chemicals such as PAHs at regional scales with simple efficiency [12].

The fugacity term is used in place of chemical potential of a substance as a thermodynamic balance to describe the fate of a chemical. Fugacity describes the exit trend of a particular chemical and similar to partial pressure. In the mass balance equation, the irregularity is used as a representation of the chemical potential [12]. Mathematically, it is described by equation (1), showing the diffusion off, and concentration of C, which is connected by a term called Z concentration; It means the tendency of an intermediate substance is to absorb another substance. With high concentration of Z, they tend to absorb more substances which results in higher concentration [13,14]. It is important to note that Z depends on the type of partition and partition coefficient.

$$C = Z \times f \quad (1)$$

In which: C: concentration (mol/m^3);
f: fugacity (Pa);
Z: concentration capacity (mol/m^3.Pa)

The mathematical "Fugacity" model has four levels. Each level represents different initial boundary hypothesis.

This simulation is elementary but useful as a preliminary assessment of chemical partitions. The level I model assume the environment was closed, stable and reaches balanced system, there are no reactions happened in this level. Level II model also assume equilibrium between all phases but the environment was an open system and stable state. These model become more realistic because they introduce the rate of chemical reaction and advection, which are represented using D_R and D_A values.

Level III model only assume equilibrium between dispersed phases rather than bulk phases. These models introduce inter-phase transfer rates and assume steady state, but non-equilibrium conditions between environmental phases. Level III models can provide value insights including chemical persistence and potential for transport between dispersed [12]. Level IV model are extension of level III model to unsteady state conditions. Mass balance equations for each phase are written in differential equations. This level is the closest one to actual environment while assuming that the environmental conditions are unstable and imbalanced. These models can be used to show time-dependent behavior of pollutant. Whereas the Level I and II model assume equilibrium status among all media, this is recognized as excessively simplistic and even misleading. In the interests of algebraic simplicity, only the four primary media are treated for this level. The task is to develop expressions for inter-media transport rates by the various diffusive and non-diffusive processes as described by Mackay (2001) [12]. Besides, Level IV models are more realistic and are used in the proposed approach. However, Level III models are the most widely used fugacity models because they are less complex and require less data.

II. STUDY METHORD

Level III fugacity model, derived from Mackay [12] was applied to simulate the fate of PAHs in Dong Rui mangrove forest and the basic model structure was recalibrated and reconfigured. The bulk compartments defined in the model were air, sediment, soil and water. Sub-compartments including gases and particles in the air, water and suspended solids, aquatic organism were taken into consideration. The processes of transfer and transformation are shown in the graphical abstract, and additional details are given in Table 1 and 2. A set of steady state mass balance equations with fugacity as the variable among the bulk compartments are listed in Table 2- 5. The transfer rate coefficients of the modeled processes and for the fugacity capacity of each compartment are presented in Table 5.

The environment in the level III fugacity model is assumed that the environment as an open system, to be stable and balanced but there is the transport of pollutants between the environmental compartments. Equilibrium equation for environmental compartments is based on the following formula:

$$\text{Input} = \text{Output}$$

The total input in this equation is defined as total of direct emission (Ei) and the discharge load from convection measured in condition where several waste sources that cannot be identified. The contaminant then moved from source to component environmental compartments thanks to the convection ($G_{Ai} \times C_{Bi}$).

$$\text{Input} = E_i + G_{Ai} \times C_{Bi}$$

Level III fugacity model describes the distribution of pollutants in environmental components when it is assumed that pollutants enter the environment with stable flow. Pollutants will be decomposition, come out of the environment by convection and transport from one compartment to another.

Output = Output for advection + Output for reaction + Transports between compartments.

Upon studying research location, we found 4 main compartments of air, water, soil and sediment. These 4 main compartments included 11 sub-compartments. In detail: The air compartment consisted of two sub-compartments: dust particles and air. The water compartment consisted of three sub-compartments: pure liquid water, suspended matter and aquatic organisms. The surface soil compartment consisted of three sub-compartments: water, air and solid particles. The sediment compartment consisted of two sub-compartments: water and solid particles.

III. DISCUSSION RESULT

Identify conditions of the fugacity distribution model combining

Environments compartment in this study is: air, soil, water and sediment. To identify the concentration (Z) of the sub-compartments, it is necessary to identify parameters related to physical and chemical properties of BaP and specific gravity of each environmental compartment. Identification of these parameters is based on references, field measurement or

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laboratory analysis. Concentration in main environmental compartments is determined on the basis of sub-compartments.

TABLE 1. The result of Z values [12,15]

Environmental compartment	Concentration (Z)
Sub-environmental compartments	
Pure air	0.000417636
Pure water	13.51351351
Dust (Aerosol particles)	2635102.373
Particles in water	1623261.883
Particles in soil	267303.6035
Particles in sediment	1549145.884
Aquatic organism	740863.646
Bulk environmental compartments	
Air (1)	0.001208166
Water (2)	21.86334038
Soil (3)	133655.8559
Sediment (4)	77470.13203

BaP contaminated mangrove forest consists of two main sources air and water. Air source formed by the combustion of raw materials, fuel. BaP will be adsorbed on dust particles. Water source formed by BaP from the air into the river water and spread to the Dong Rui mangroves. There are no emission in Dong Rui mangroves.

TABLE 2. Input value

Compartment	$G_{Ai}\ C_{Bi}$ (mol/h.Pa)
Air	0.599286564
Water	0.093788347

When BaP enters the mangroves, they will be distributed in all four compartments of land, water, air, and sediment. In each compartment, part of it decomposes, partially out of the mangroves, partially into other environmental compartments and partially accumulating in the environment.

TABLE 3. Output value for advection

Air compartment	D_{Ai} (mol/h.Pa)
Air	108734966.4
Water	165286853.3

TABLE 4. Output value for reaction [12,15]

Compartment	D_{Ri} (mol/h.Pa)
Air	453105.0011
Water	401063.6881
Soil	15255636.63
Sediment	1757022.594

TABLE 5. Intermedia transfer D [12,15]

Symbol	Process	Unit	Value
D12	Air- water	mol/h.Pa	185242.438
D21	Water- Air	mol/h.Pa	108137.4
D13	Air- Soil	mol/h.Pa	126476.7948
D31	Soil- Air	mol/h.Pa	6535.624674
D23	Water- soil	mol/h.Pa	3666715295
D32	Soil- Water	mol/h.Pa	1.31119E+12
D24	Water- sediment	mol/h.Pa	14648710.96
D42	Sediment- water	mol/h.Pa	5616279.195

Distribution BaP in environment compartments

We have equilibrium equation for compartments as described below:

For air compartment:

$0 = G_{A1}\,C_{B1} + f_2\,D_{21} + f_3 D_{31} - f_1(D_{13} + D_{12} + D_{R1} + D_{A1})$

f_1 x 2064538.478 = f_2 x 1040.872134 + f_3 x 156.6391276 + 0.006592152 (2)

For water compartment:

$0 = G_{A2}\,C_{B2} + f_1 D_{12} + f_3 D_{32} + f_4 D_{42} - f_2\,(D_{21} + D_{23} + D_{24} + D_{R2} + D_{A2})$

f_2 x 82092471778 = f_1 x 1043.21823 + f_3 x 37114211050 + f_4 x 12182451167 + 0.00019 (3)

For soil compartment:

$0 = f_1\,D_{13} + f_2\,D_{23} - f_3(D_{31} + D_{32} + D_{R3})$

f_3 x 4.9791E+11 = f_1 x 2006.685013 + f_2 x 35037446278 (4)

For sediment compartment:

$0 = f_2\,D_{24} - f_4\,(D_{42} + D_{R4})$

f_4 x 4.63167E+11 = f_2 x 33907821209 (5)

The results of BaP distribution in each environmental compartment were characterized by the solution of above four equation. BaP transfers and reservoirs predicted by level III are depicted in Figure 1. The table 6 summarizes the estimated results about the BaP distribution in each environmental compartment. The results show that the BaP can be accumulated majority in the soil and sediment. The percentage of BaP distribution achieve at 53.2% in soil, followed by sediment of 46.4%, Air (0.19%) and Water (0.16%). This result agrees with previous study when defined that the BaP existence is almost in sediment and soil, but the distribution among air and water was inverse [10*]. This result is logical in the Dong Rui mangroves due to the tidal phenomenon and the BaP deposition from the sources of the Mong Duong thermal power plant and nearby areas. Reaction residence time is estimated at 27663.7 h While advection residence time is 525.6 h and Total residence time is 451.4 h. Thus, reaction residence time is very high, meaning that BaP can be considered as resistant in the environment and hardly to react. The percentage of reaction in each environmental component is: 0.36% (air), 0.03% (water), 0.9% (soil), 0.2% (sediment). The percentage of advection in each environmental component is: 85.9% (air), 12.5% (water). Dong Rui mangrove forests reduce pollutant load mainly due to the convection process whereas, the decomposition process doesn't contribute in pollutant reduction in the environment.

To assess the uncertainty of the Level III model results, The simply methodology used to test is to assume that, if total input is equal to total output, the estimated results can be accepted.

Basing on the results in table 6 and comparing the total input and output load, the estimated method is acceptable

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Total input = $G_{A1}x\ C_{B1} + G_{A2}x\ C_{B2}$ = 0.693074911 mol/h

Total output = Total decomposited load + Total advective load = 0.693074911 mol/h.

IV. CONCLUSION

PAHs were enriched in Dong Rui mangroves forest with special terrain from the deposition of Particles, gas phase and water bodies. The BaP were accumulated majority in soil of mangrove. Fugacity Level III can desrible BaP distribution in each environmental compartment and conclude that BaP can exist almost in soil and sediment, follow by air and water. Reaction residence time is greatest. Dong Rui mangrove forests reduce the pollutant load mainly due to the convection process, because BaP is a durable organic compound in the environment. The estimated results of model is acceptable.

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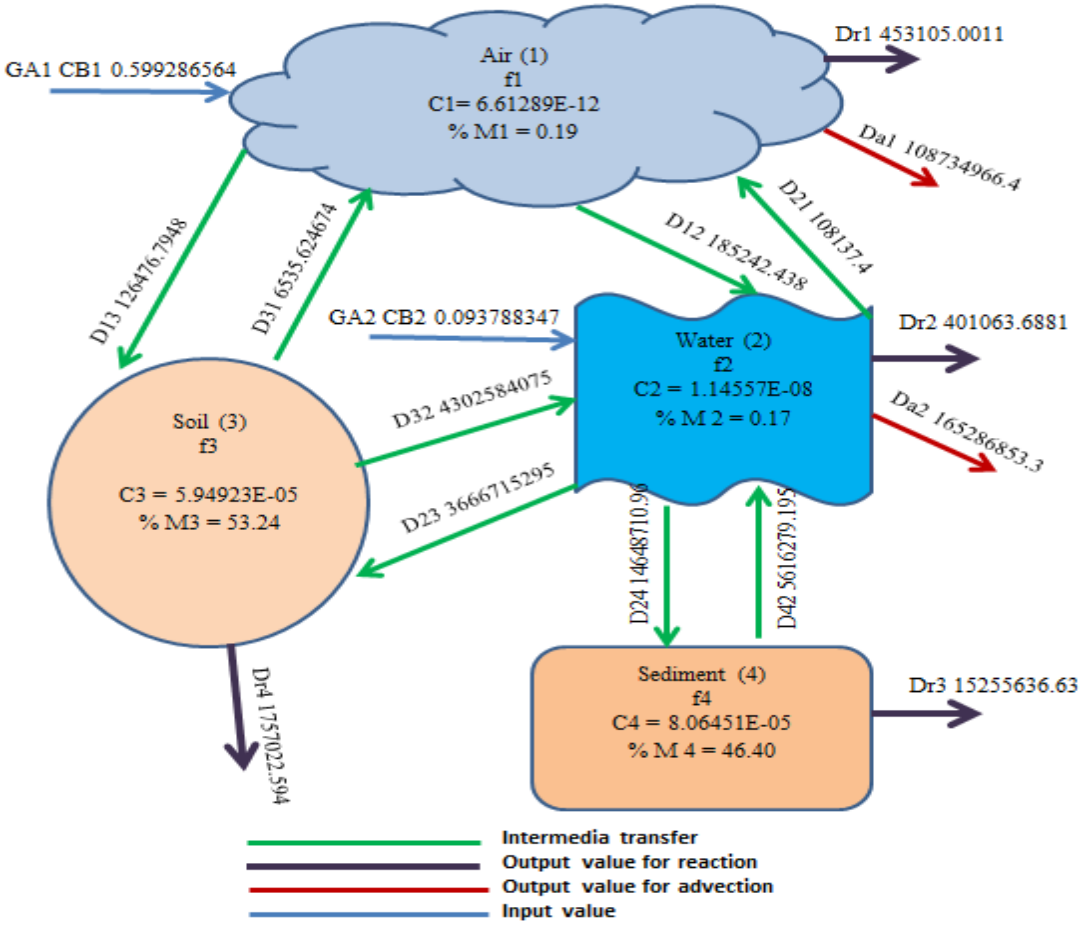

Figure 1: Distribution intermedia transport D values

TABLE 6. Result of BaP distribution in each environmental compartment

Index	Unit	Air compartment	Water compartment	Soil compartment	Sediment compartment	Total
f	Pa	5.47349E-09	5.23979E-10	4.45011E-10	1.041E-09	
Z	mol/m3.Pa	0.001208166	21.86334038	133655.8559	77470.13203	
C	mol/m3	6.61289E-12	1.14559E-08	5.94784E-05	8.06465E-05	
V	m3	92000000000	45000000	2800000	1800000	
M	mol	0.60838565	0.515516829	166.5394261	145.1636965	312.8270251
% M	%	0.194479889	0.164792933	53.23690498	46.4038222	
Total input	mol/h	0.599286564	0.093788347	0	0	0.693074911
Overall residence time	h	451.3610581				
Output by reaction	mol/h	0.002480066	0.000210149	0.006788931	0.001829063	0.011308208
Output by advection	mol/h	0.595159875	0.086606827			0.681766702
Total output	mol/h					0.693074911
Reaction residence time	h	27663.71235				
Advection residence time	h	525.6184736				
% Reaction	%	0.357835231	0.030321242	0.979537798	0.263905466	
% Advection	%	85.87237336	12.4960269			