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RESEARCH ON ENVIRONMENTAL FATE OF PHENANTHRENE IN LANZHOU REACH OF YELLOW RIVER

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Model Assumptions

According to the environmental characteristics of Lanzhou Reach, the environmental system is divided into four subsystems including air, water, suspending substances (SS) and bottom sediment (SS) and there is non-equilibrium between any two different subsystems. It is also supposed that air is composed of gas phase and solid phase between which the equilibrium exists, while bottom sediment is composed of solid phase and liquid phase between which the equilibrium exists.

Model Mechanisms

The input processes of phenanthrene include source emissions, mass transfers by advective inflows, diffusion processes and non-diffusion processes from other media. The output processes of phenanthrene include mass transfers by advective outflows, diffusion processes and non-diffusion processes to other environmental media and degrading reactions.

Model Equations

Under unsteady state, the mass balance method is used to assemble four differential equations (1) to (4) to describe behaviors of phenanthrene in air, water, SS and BS.

$$V_1 Z_1 \frac{df_1}{dt} = E_1 + G_{1I} Z_1 f_{1I} + D_{21} f_2 - (G_{1O} Z_1 + D_{12} + D_{13} + r_1 V_1 Z_1) f_1 \quad (1)$$

$$V_2 Z_2 \frac{df_2}{dt} = E_2 + G_{2I} Z_2 f_{2I} + D_{12} f_1 + D_{32} f_3 + D_{42} f_4 - (G_{2O} Z_2 + D_{21} + D_{23} + D_{24} + r_2 V_2 Z_2) f_2 \quad (2)$$

$$V_3 Z_3 \frac{df_3}{dt} = E_3 + G_{3I} Z_3 f_{3I} + D_{13} f_1 + D_{23} f_2 + D_{43} f_4 - (G_{3O} Z_3 + D_{32} + D_{34} + r_3 V_3 Z_3) f_3 \qquad (3)$$

$$V_4 Z_4 \frac{df_4}{dt} = E_4 + G_{4I} Z_4 f_{4I} + D_{24} f_2 + D_{34} f_3 - (G_{4O} Z_4 + D_{43} + D_{BS} + r_4 V_4 Z_4) f_4 \qquad (4)$$

where subscript i=1, 2, 3, 4 represents air, water, SS and BS, respectively. f_i is the fugacity of phenanthrene in media i (Pa), Z_i is the fugacity capacities of phenanthrene in media i (mol•m^{-3}•Pa^{-1}), V_i is the volume of media i(m^3), E_i is the emission of phenanthrene in media i (mol•h^{-1}), G_{iI} is the inflow rate of media i(m^3•h^{-1}), f_{iI} is the fugacity of phenanthrene in inflows of media i (Pa), G_{iO} is the outflow rate of media i (m^3•h^{-1}) and r_i is the reaction rate constant of phenanthrene in media i (h^{-1}).

Equations (1)-(4) can be expressed as the following matrix equation:

$$\dot{f} = A \cdot f(t) + I \cdot U(t) \qquad (5)$$

where $\dot{f} = \begin{pmatrix} \frac{df_1}{dt} \\ \frac{df_2}{dt} \\ \frac{df_3}{dt} \\ \frac{df_4}{dt} \end{pmatrix}$, $f(t) = \begin{pmatrix} f_1(t) \\ f_2(t) \\ f_3(t) \\ f_4(t) \end{pmatrix}$, $I = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$, $A = \begin{pmatrix} a_{11} & \frac{D_{21}}{V_1 Z_1} & 0 & 0 \\ \frac{D_{12}}{V_2 Z_2} & a_{22} & \frac{D_{32}}{V_2 Z_2} & \frac{D_{42}}{V_2 Z_2} \\ \frac{D_{13}}{V_3 Z_3} & \frac{D_{23}}{V_3 Z_3} & a_{33} & \frac{D_{43}}{V_3 Z_3} \\ 0 & \frac{D_{24}}{V_4 Z_4} & \frac{D_{34}}{V_4 Z_4} & a_{44} \end{pmatrix}$,

$$U(t) = \begin{pmatrix} \frac{E_1 + G_{1I} Z_1 f_{1I}}{V_1 Z_1} \\ \frac{E_2 + G_{2I} Z_2 f_{2I}}{V_2 Z_2} \\ \frac{E_3 + G_{3I} Z_3 f_{3I}}{V_3 Z_3} \\ \frac{E_4 + G_{4I} Z_4 f_{4I}}{V_4 Z_4} \end{pmatrix}, \qquad a_{11} = \frac{-(G_{1O} Z_1 + D_{12} + D_{13} + r_1 V_1 Z_1)}{V_1 Z_1},$$

$$a_{22} = \frac{-(G_{2O} Z_2 + D_{21} + D_{23} + D_{24} + r_2 V_2 Z_2)}{V_2 Z_2}, \qquad a_{33} = \frac{-(G_{3O} Z_3 + D_{32} + D_{34} + r_3 V_3 Z_3)}{V_3 Z_3},$$

$$a_{44} \frac{-(G_{4O} Z_4 + D_{43} + D_{BS} + r_4 V_4 Z_4)}{V_4 Z_4}$$

Calculations of Input Parameters

Fugacity Capacities of Phenanthrene in Different Environmental Media

Table 1. Fugacity capacities of phenanthrene in different environmental media.

environmental media	Volume (m^3)	fugacity capacities ($mol \bullet m^{-3} \bullet Pa^{-1}$)
air	6.624E9	Z_1=4.236E-4
water	3.312E7	Z_2=7.5988E-3
SS	18348	Z_3=5.4172
BS	6.624E5	Z_4=0.29827

Transfer Rate Constants of Phenanthrene (see Table 2).

Table 2. Transfer rate constants of phenanthrene.

environmental media	transfer rate constants ($mol \bullet h^{-1} \bullet Pa^{-1}$)
air—water	D_{12}=2564.4
air—SS	D_{13}=19.671
water—air	D_{21}=2560.6
water—SS	D_{23}=5740.2
water—BS	D_{24}=10.067
SS—water	D_{32}=5740.2
SS—BS	D_{34}=35.883
SS—water	D_{42}=10.067
BS—SS	D_{43}=2.587
vertical burying process	D_{BS}=12.937

SS-suspending substances, BS-bottom sediment.

Rate Constants of Inflow and Outflow (see in table 3).

Table 3. Inflow rate constants and outflow rate constants.

environmental media	inflow ($mol \cdot h^{-1} \cdot Pa^{-1}$)	outflow ($mol \cdot h^{-1} \cdot Pa^{-1}$)
air	$D_{1I}=G_{1I} \cdot Z_1=0$	$D_{1O}=G_{1O} \cdot Z_1=0$
water	$D_{2I}=G_{2I} \cdot Z_2=387.54$	$D_{2O}=G_{2O} \cdot Z_2=350.47$
SS	$D_{3I}=G_{3I} \cdot Z_3=153.09$	$D_{3O}=G_{3O} \cdot Z_3=138.41$
BS	$D_{4I}=G_{4I} \cdot Z_4=0$	$D_{4O}=G_{4O} \cdot Z_4=0$

Solution of Fugacity Model

Solution of Steady State

The initial state vector of phenanthrene is $f(0)=\begin{pmatrix} f_{10} \\ f_{20} \\ f_{30} \\ f_{40} \end{pmatrix}=\begin{pmatrix} 0.00472 \\ 7.71E-4 \\ 2.596E-3 \\ 4.75E-4 \end{pmatrix}$ and the emissions in each media are $E_1 = 6.9352 mol/h$, $E_2 = 0.4689 mol/h$, $E_3 = 7.275 mol/h$ and $E_4 = 0$.

The steady solution is $f = -A^{-1}U = \begin{pmatrix} 0.0473 \\ 0.0450 \\ 0.0464 \\ 0.1365 \end{pmatrix}$. So the final distributions of phenanthrene in Lanzhou Reach can be seen in Table 4.

Table 4. Final distributions of phenanthrene in Lanzhou Reach.

environmental media	Fugacity (Pa)	Total mass (kg)	Percent (%)
air	0.0473	23655.5	75.570
water	0.0450	2018.16	6.448
SS	0.0464	821.84	2.626
BS	0.1365	9526.28	15.356
total	—	31296.61	100

Numerical Simulation and Results

The integral solution of Eq.(5) is $f(t)=\exp(At)\cdot f(0)+\int_0^t \exp(A(t-\tau))\cdot I\cdot U(\tau)d\tau$; its discrete form is

$$f((k+1)\Delta t)=W(\Delta t)f(k\cdot\Delta t)+H(\Delta t)U(k\cdot\Delta t) \quad (6)$$

where $k\in Z^{+}$, $W(\Delta t)=\exp(A\cdot\Delta t)$, $H(\Delta t)=\int_0^{\Delta t}\exp(A\tau)I\cdot d\tau$.

The changes of phenanthrene in Lanzhou Reach are simulated by using Matlab 6.5 according to Eq. (6). The simulations can be seen in Table 5.

Table 5. Numerical simulation of phenanthrene in Lanzhou Reach.

Time (10^3h)	Fugacity (Pa)				total mass (kg)			
	air	water	SS	BS	air	water	SS	BS
0	4.72E-3	7.71E-4	2.596E-3	4.75E-4	2360.1	34.6	46	16.7
5	0.0047	0.0008	0.0026	0.0005	12401	1142	483	675
10	0.0248	0.0255	0.0273	0.0192	17573	1540	637	1540
15	0.0351	0.0343	0.036	0.0437	20217	1745	716	2334
20	0.0404	0.0389	0.0404	0.0663	21619	1855	759	2982
25	0.0432	0.0414	0.0429	0.0847	22394	1917	783	3479
30	0.0448	0.0427	0.0442	0.0988	22842	1953	797	3850
35	0.0457	0.0435	0.045	0.1093	23113	1975	805	4121
40	0.0462	0.044	0.0455	0.117	23283	1989	811	4316
45	0.0466	0.0443	0.0458	0.1226	23394	1998	814	4457
50	0.0468	0.0445	0.046	0.1266	23467	2004	817	4557
55	0.0469	0.0447	0.0461	0.1294	23518	2008	818	4629
60	0.047	0.0448	0.0462	0.1315	23552	2011	819	4680
65	0.0471	0.0448	0.0463	0.1329	23576	2013	820	4716
70	0.0472	0.0449	0.0463	0.1339	23593	2014	821	4741
75	0.0472	0.0449	0.0463	0.1347	23605	2015	821	4759
80	0.0472	0.0449	0.0464	0.1352	23613	2016	821	4772
∞	0.0473	0.0450	0.0464	0.1365	23651	2018	822	4806

From Table 5, it can be seen that the changing rates of phenanthrene in air, water and SS are approximate, while it changes more slowly in BS. The contents of phenanthrene in air, water and SS will be steady in 45,000 hours, while it takes about 70,000 hours to be steady in BS. The final fugacities of phenanthrene in air, water, SS and BS in Lanzhou Reach are 0.0473Pa, 0.0450Pa, 0.0464Pa and 0.1365Pa, respectively. The total mass of phenanthrene in each media is 23,651kg, 2,018kg, 822kg and 4,806kg, respectively with the corresponding percent of 76%, 6%, 3% and 15%.

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