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Application of Markov model to environmental fate of phenanthrene in Lanzhou Reach of Yellow River

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Abstract

The theory of Markov Chain is used scientifically to describe the transfer/transformation of phenanthrene in Lanzhou Reach of Yellow River. In Markov Model (MM), the states of phenanthrene in Lanzhou Reach are divided into six different states, namely being degraded, leaving the system with the addvective flow, being in air, being in water, being adsorbed on suspending substances (SS), and being in bottom sediment (BS).

The MM is simulated by using Matlab6.5 to reveal the temporal changes and environmental fate of phenanthrene in Lanzhou Reach. It is shown that the environmental system will be steady in 30000–35000 h, the final distributions of phenanthrene in air, water, SS, and BS are 23033 kg, 1961 kg, 800 kg, and 2824 kg respectively, with the corresponding percent of 80%, 7%, 3%, and 10%.The results of MM are approximate to the results of Fugacity Model (FM), so Markov Chain can be used to evaluate the environmental fate of pollutants in multimedia environment.

The outputs of MM include the following aspects: (1) The residual time of pollutant in different environmental media and the transiting time of pollutant between different environmental media; (2) The response time of the environmental system; (3) The total mass of pollutant transferred or degraded during a given time interval; (4) The time needed for the environmental system to be steady and the final steady distributions of pollutant in the environmental system.

Keywords: Theory of Markov Chain; Environmental fate; Phenanthrene; Lanzhou Reach of Yellow River

1. Introduction of Markov Chain

Markov Chain is an important random process, its theory lies in using transition matrix to describe the transitions of a substance among different states. If the substance has all together n different kinds of states, which are expressed as $i = 1, 2, \ldots, n$, the transition matrix would be described as the following matrix:

$$P = \begin{pmatrix} p_{11} & p_{12} & \cdots & p_{1n} \\ p_{21} & p_{22} & \cdots & p_{2n} \\ \cdots & \cdots & \cdots & \cdots \\ p_{n1} & p_{n2} & \cdots & p_{nn} \end{pmatrix},$$

where the element p_{ij} in the matrix is the transition probability for the substance transiting from state i to state j in each unit time. Supposing the initial state vector of the substance is $T^{(0)} = (y_{10}, y_{20}, \ldots, y_{n0})$, at k time, the state vector will be $T^{(k)} = T^{(0)} \cdot P^k$.

Markov Chain has been applied to agriculture (Hudson and Bienie, 2000; Meza and Wilks, 2004), forestry (Schlicht and Iwasa, 2004), biology (Yakowitz, 1995; Bahi-Jaber and Pontier, 2003; Johnson et al., 2004), medicine (Singer and Younossi, 2001; Hlavacek et al., 2002), business (Wei, 2003; Wu, 2005) and chemical enginering (Cheng and Duran, 2004; Berthiaux et al., 2005) widely. In environmental protection, Markov Chain has been used to evaluate the operation of environmental facilities (Zhang, 1997), and the transportation of pollutants along food chain in ecological system (Harmon and Challenor, 1997). But it has not been used to evaluate the environmental fate of chemicals in

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multimedia environment. So, for the first time, this thesis tries to use Markov Chain to evaluate the environmental fate of phenanthrene in Lanzhou Reach of Yellow River.

2. Applications of Markov Chain to the environmental fate of pollutants

In environment, pollutants can exist in different environmental media, transfer among the environmental media, leave away or disappear from the environment because of advective flow or degrading reactions. The state of leaving or disappearing forever is called absorbing state, while non-absorbing state is called transient state (usually named environmental media), and the transition probability of pollutant from any absorbing state to any transient state is zero. Usually the changing process of pollutant in environment is an absorbing Markov Chain, supposing the pollutant has k kinds of transient states (i.e. the pollutant exists in k different kinds of environmental media), and r absorbing states, then its transition matrix can be described as the following canonical form:

$$P = \begin{pmatrix} I_{r\times r} & 0_{r\times k} \\ R_{k\times r} & Q_{k\times k} \end{pmatrix},$$

where $I_{r\times r}$ – the transition matrix from absorbing states to absorbing states, so its diagonal elements are 1, others are zeroes, $0_{r\times k}$ – the transition matrix from absorbing states to transient states, so each element in $0_{r\times k}$ is zero, $R_{r\times k}$ – the transition matrix from transient states to absorbing states, $Q_{k\times k}$ – the transition matrix from transient states to transient states.

According to the property of absorbing Markov Chain, the fundamental matrix is $N = (I_{k\times k} - Q_{k\times k})^{-1} = (n_{ij})_{k\times k}$, the element n_{ij} in matrix N expresses the time needed for pollutants to transit from the transient state i to the transient state j before it leaves or disappears forever. The expression $t_i = \sum_{j=1}^{k} n_{ij}$ is the time needed for the pollutant in transient state i to transfer into all other transient states before it leaves or disappear forever. Let $B = N \cdot R = (b_{ij})$, then b_{ij} expresses the ratio of pollutant in transient i transiting to absorbing state j.

Let $E_i(t)$ be the source emission of phenanthrene into environmental media i (or transient state i), then the changing rules of phenanthrene in different time can be expressed as the following formulas:

$$T^{(0)} = (Y^{(0)} X^{(0)}), \tag{1}$$

$$T^{(t+1)} = T^{(t)}P + (0E(t+1)) \quad (t = 1, 2, \ldots), \tag{2}$$

where $X^{(0)} = (x_1\ x_2 \cdots x_k)$ – the initial transient state vector, $Y^{(0)} = (y_1\ y_2 \cdots y_r)$ – the initial absorbing state vector, P – the transition matrix.

Those above formulas can be arranged as the following expression:

$$T^{(t)} = \begin{pmatrix} Y^{(t)} & X^{(t)} \end{pmatrix} = \left(Y^{(0)} + X^{(0)}R_t + \sum_{i=1}^{t} E(i)R_{t-i} \quad X^{(0)}Q^{(t)} + \sum_{i=1}^{t} E(i)Q^{t-i} \right), \tag{3}$$

where $R_t = (E - Q^t)(E - Q)^{-1}R$.

According to the above mentioned theory, the outputs of Markov Chain include: (1) the residual time of pollutant in different environmental media and the transiting time of pollutant between different environmental media, (2) the response time, which is the time needed for the environmental system to obtain a certain level after the source emission stops or the source emission reduces, (3) the transferring mass and the degraded mass of pollutant during a given time interval, (4) the time needed for the environmental system to be steady and the final steady distribution of pollutant in the environmental system.

3. Environmental fate of phenanthrene in Lanzhou Reach of Yellow River

3.1. Inputs of initial states of phenanthrene and source emissions

In Lanzhou Reach, the states can be classified into six states, namely being in air, being in water, being in SS, being in BS, being degraded, and leaving the system because of advective flow. The last two states are absorbing states, others are transient states.

According to the environmental monitoring and experimental analysis, the initial absorbing state vector is $Y^{(0)} = (0\ 0)$ (kg), the initial transient state vector is $X^{(0)} = (2360\ 34.58\ 45.98\ 16.72)$ (kg), the source emission vector of phenanthrene is $E = (1235.9\ 128.44\ 266.15\ 0)$ (gh^{-1}).

3.2. Transferring characteristic of phenanthrene in Lanzhou Reach

On basis of property of Lanzhou Reach and physicochemical property of phenanthrene, its transition matrix in Lanzhou Reach is

$$P = \begin{pmatrix} I & 0 \\ R & Q \end{pmatrix},$$

where

$$I = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad R = \begin{pmatrix} 0 & 0 \\ 0 & 1.393E-3 \\ 0 & 1.3925E-3 \\ 0 & 6.5661E-5 \end{pmatrix},$$

$$Q = \begin{pmatrix} 0.99908 & 9.1392E-4 & 7.01E-6 & 0 \\ 1.0174E-2 & 0.96558 & 2.2808E-2 & 4E-5 \\ 0 & 5.77515E-2 & 0.94049 & 3.61E-4 \\ 0 & 5.095E-5 & 1.3095E-5 & 0.99987 \end{pmatrix}.$$

Table 1
Residual time and transiting time of phenanthrene (h)

Environmental media	Transiting time				Residual time
	Air	Water	SS	BS	
Air	–	496.3	191.2	683.5	1371.0
Water	5484.5	–	190.9	682.6	6358
SS	5338.7	482.8	–	711.2	6532.7
BS	2687.3	243	95.2	–	3025.5

Table 2
Stimulation of phenanthrene in Lanzhou Reach (kg)

Time (1000 h)	Degraded	Leaving	In air	In water	In SS	In BS
0	0	0	2360	34.58	45.98	16.72
5	0	7943	12407	1141	483	610
10	0	21698	17569	1538	636	1287
15	0	38429	20174	1739	714	1823
20	0	56727	21512	1842	754	2196
25	0	75863	22213	1897	775	2440
30	0	95453	22585	1926	786	2593
35	0	115290	22790	1940	790	2690
40	0	135270	22900	1950	800	2740
45	0	155330	22960	1960	800	2780
50	0	175430	22990	1960	800	2800
55	0	195550	23010	1960	800	2810
60	0	215690	23020	1960	800	2810
65	0	235830	23030	1960	800	2820
70	0	255980	23030	1960	800	2820
75	0	276140	23030	1960	800	2820
80	0	29629	23030	1960	800	2820
∞	0	∞	23033	1961	800	2824

Table 3
Steady distribution of phenanthrene in Lanzhou Reach

Environmental media	Concentration	Total mass (kg)	Percentage (%)
Air	3.48 $\mu g\,l^{-1}$	23033	80.48
Water	59.24 $\mu g\,l^{-1}$	1961	6.85
SS	17.01 $mg\,kg^{-1}$	800	2.80
BS	4.26 $mg\,l^{-1}$	2824	9.87
Total	–	28618	100

So the fundamental matrix is

$$N = (I - Q)^{-1} = \begin{pmatrix} 6575.9 & 496.3 & 191.2 & 683.5 \\ 5484.5 & 495.9 & 190.9 & 682.6 \\ 5338.7 & 482.8 & 202.6 & 711.2 \\ 2687.3 & 243 & 95.2 & 8031.5 \end{pmatrix}.$$

From matrix N, the residual time of phenanthrene in each environmental media and the transiting time of phenanthrene between any two environmental media can be obtained (in Table 1).

From Table 1 it can be seen that the residual times of phenanthrene in air, water, SS, and BS in Lanzhou Reach are 1371 h, 6358 h, 6532 h, and 3025 h respectively, so the residual time in air is the shortest.

3.3. Temporal changes of phenanthrene in Lanzhou Reach

On basis of data in Sections 3.1 and 3.2, expression (3) is simulated to reveal the changes of phenanthrene in Lanzhou Reach, by using Matlab6.5 (in Table 2).

From Table 2, it can be seen that the changing rate in air is the biggest, the changing rate in BS is the second biggest,

Table 5
Comparisons of the steady distribution between MM and FM

		Time needed to be steady (h)	Steady concentration	Steady content (kg)	Steady proportion (%)
Air	FM	45000–50000	3.57 $\mu g\,l^{-1}$	23651	75.57
	MM	35000	3.48 $\mu g\,l^{-1}$	23033	80.48
Water	FM	45000	60.93 $\mu g\,l^{-1}$	2018	6.45
	MM	35000	59.24 $\mu g\,l^{-1}$	1961	6.85
SS	FM	45000	17.48 $mg\,kg^{-1}$	821.84	2.63
	MM	35000	17.01 $mg\,kg^{-1}$	800	2.80
BS	FM	70000–75000	7.255 $mg\,l^{-1}$	4806	15.35
	MM	50000	4.26 $mg\,l^{-1}$	2824	9.87

Table 4
Simulation comparison between MM and FM (kg)

Time (1000 h)	Air		Water		SS		BS	
	MM	FM	MM	FM	MM	FM	MM	FM
0	2360	2360.1	34.58	34.6	45.98	46	16.72	16.7
5	12407	12401	1141	1142	483	483	610	675
10	17569	17573	1538	1540	636	637	1287	1540
15	20174	20217	1739	1745	714	716	1823	1823
20	21512	21619	1842	1855	754	759	2196	2982
25	22213	22394	1897	1917	775	783	2440	3479
30	22585	22842	1926	1953	786	797	2593	3850
35	22790	23113	1940	1975	790	805	2690	4121
40	22900	23283	1950	1989	800	811	2740	4316
45	22960	23394	1960	1998	800	814	2780	4457
50	22990	23467	1960	2004	800	817	2800	4557
55	23010	23518	1960	2008	800	818	2810	4629
60	23020	23552	1960	2011	800	819	2810	4680
65	23030	23576	1960	2013	800	820	2820	4716
70	23030	23593	1960	2014	800	821	2820	4741
75	23030	23605	1960	2015	800	821	2820	4759
80	23030	23613	1960	2016	800	821	2820	4772

and the changing rate in SS is the smallest. Since the initial time, the distributions of phenanthrene in Lanzhou Reach will be steady in about 30000–35000 h.

According to the property of Markov Chain, the final distribution of phenanthrene in Lanzhou Reach is $T = E \cdot N = (23033\ 1961\ 800\ 2824)$. So the final steady contents, concentration and percentage of phenanthrene in Lanzhou Reach of Yellow River can be seen in Table 3.

From Table 3, it can be seen that air will be the main carrying media for phenanthrene in the future, the reason may lie in the natural geographical conditions.

4. Conclusions

In order to testify the efficiency and accuracy of Markov Chain, the outputs of MM and FM are compared (in Tables 4 and 5). The reason that FM is used to testify the efficiency and accuracy of MM lies in that there are not adequate monitor data and FM has been used widely and successfully in environmental fate of chemicals.

From Table 4, it can be seen that the simulations of two different models are approximate, except the outputs of BS.

From Table 5, it can be seen that the FM need more time to be steady, but their steady concentrations of phenanthrene in Lanzhou Reach is approximate, except the BS. The reason may lie in the different structures of two models.

In spite of the differences, Markov Chain is scientific and reasonable, it can be used to evaluate the environmental fate of pollutants in multimedia environment.

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