The study for polyaromatic hydrocarbons decay on Chinese coal soot particles in atmosphere[*]

Shu Yonghui[1], Li Jinhua[1] and Wang Wenxing[1]

Abstract — A study for the photochemical behavior of some polyaromatic hydrocarbons (PAH), for example B(a)P, B(k)F and fluoranthene in coal smoke particles was performed by using indoor Teflon smog chamber. Experiments suggest that the photochemical reaction of PAH is first order reaction and kinetic rates of some PAH were obtained. It was shown that the reaction rate constant is proportional to light intensity and water vapor concentration. Temperature and PAH loading also have influence on PAH decay rate. A model for PAH loss has been set up on the basis of the results of our experiments and the simulating results of this model suggest that coal particle PAH half lives are of the order of a period of days in winter and a few hours in summer. Other factors which may have effect on the photochemical reaction of PAH have also been discussed.

Keywords: PAH; photochemical reaction; smog chamber; kinetic rates.

PAHs are very important species present on the soot particle. Study have demonstrated their carcinogenic effect in experimental animals (Shabad, 1980).

A lot of experiments had been conducted to study the PAH on carbon black, silica, alumina, glass fiber filter and other substances. But PAH shows different behavior on different substances. In order to estimate the realistic atmosphere behavior of PAH, Kames *et al*. had carried out studies about PAH behavior on residential wood smoke (Kames, 1985a; 1985b; 1988). Less information is available on coal soot particle PAH. Since coal burning is a major source of energy in China, studies which involved PAH behavior on particles generated by burning Chinese coal are desired.

EXPERIMENTS

Experiments were conducted in a three cubic meter Teflon smog chamber which use black-light fluorescent lamp as its light source. The chamber system, stove injection manifold and
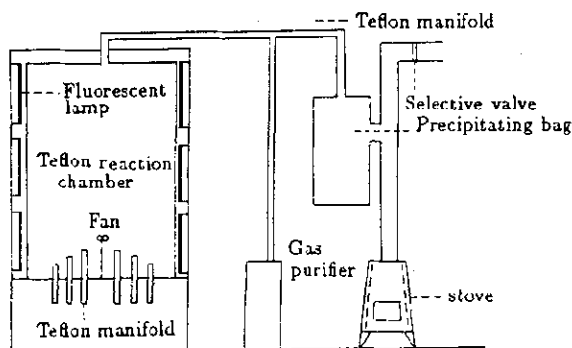
sampling apparatus are illustrated in Fig. 1.

Fig. 1   Illustration of Teflon film chamber and associated systems

At the bottom of the chamber, there are six sampling manifolds. Three of them are individually used for measuring O_3, NO_x, temperature and humidity. The other of them are used for aerosol sampling.

In order to attain the realistic atmosphere condition, the transmissivity picture of the lamp is similar to that of sunlight in UV section which plays most important part in photochemical reaction. The light intensity of the lamp can be adjusted between 0 to 74.5 $\mu w/m^2$.

In order to prevent large particles ($> 0.5 \mu m$) from entering reaction chamber, original coal smoke was first injected into a precipitating Teflon bag, for particles with size less than 0.4 μm constitute most of the particles in realistic atmosphere. The precipitation bag is completely covered with black cloth so no undesire reaction caused by exposing to light will occur before smoke is infected into the reaction chamber. The precipitating time is about half an hours. Before experiment, the reaction chamber was washed with purified gas until the concentration of NO_x and O_3 was less than 1 ppb. Then the smoke in the precipitating bag was induced into the reaction chamber from top of the chamber by exhausting air at the bottom of chamber. In order to avoid any effect that NO_x and O_3 may have on PAH decay, the amount of smoke being induced into the reaction chamber should be confined less than 9 mg, thus NO_x and O_3 concentration in the chamber will be limited individually below 0.07 and 0.2 ppm. A Teflon-coated fan which is situated at the bottom of the chamber was used to mix the gas in the chamber. After the smoke was well-distributed, about 0.2 microgram particles were collected by drawing air through a Teflon filter film. After taking this initial filter sample, 2.8 −8.8 mg of particles will remain in the chamber. These particles were aged in the presence of light. At different reaction time, samples were collected on Teflon filter. Five to six filter samples will be collected during the 2 − 3 hour experiment. Teflon filter was used because it was inert to PAH reactants and collected more than 90% of the particles in air.

During experiments, the total aerosol concentration was monitored with an condensation nuclei counter (CN) and Thermo System Inc., Model 3030 electric aerosol analyzer (EAA). The particle size distribution remain same among almost all of the experiments except those with high loadings.

Coal smoke particles were then extracted from Teflon filter into dichloromethane by Ultrasonic Vibration. The extracted dichloromethane solution was concentrated to less than 1 ml with dry nitrogen stream under low pressure. In order to prevent PAH from decomposing in the solvent, all the above experiments were conducted under weak or yellow light surroundings.

The coal extract was analyzed with Varian Vista 5500 High Pressure Liquid Chromatography and fluorescent detector. The typical sample chromatogram is shown in Fig. 2.
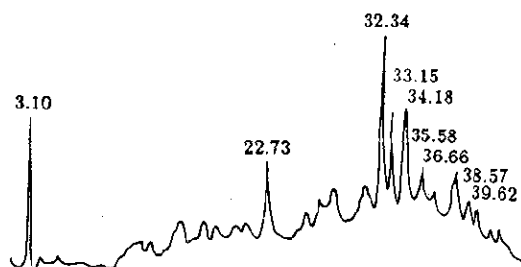

Fig.2 The chromatogram of coal soot extract

Column: Micropak SP C-18 150 × 4.6 mm

Mobile phase:

A —methanol B —water   30%A, 70%B to 100%B in 30 minutes and maintained to the end.

Flow rate: 0.7 ml/min in the first 40 min., then increased to 1.5ml/min in two minutes and lasted to the finish

Five peaks were recognized by adding standard sample into particle extract and reaffirmed by comparing the fluorescence scanning picture of sample with standard sample. The qualitative results are shown in Table 1.

Table 1   The qualitative results of particle extract

Retention time, min	Corresponding compound
22.73	fluoranthene(FLU)
32.34	benzo(b)fluoranthene+perylene (B(b)F+Pery)
33.15	benzo(k)fluoranthene(B(k)F)
34.18	benzo(a)pyrene(B(a)P)
38.57	benzo(ghi)perylene(B(ghi)P)

External standard method is used to qualitative the amount of chromatogram peaks.

RESULTS AND DISCUSSION

After adding coal smoke into the chamber, the initial NO_x concentration ranged from 0.06 to 0.08 ppm and photochemically generated ozone less than 0.09 ppm. Initial PAH loading on coal soot particle and particle concentration ranged individually from 300 to 2000 ng/mg and from 600 to 3000 $\mu g/m^3$. The solar intensity ranged from 0 to 1.03 cal . min^{-1} . cm^{-2}. During the experiments, it was shown that the particle size distribution mainly ranges from 0.1 to 0.4 μm and vary slightly with time and particles tend to became smaller. The influence of particle size distribution can be omitted comparing with the influence of other factors like light intensity and water vapor concentration on PAH loss. The data from 19 individual coal soot experiments suggest that the first two hours reaction of PAH is first order reaction.

PAH decay and sunlight, humidity

In Fig. 3 we have plotted several PAH decay rate constants vs the solar intensities for a set of experiments which occurred under different light intensities and approximated to the chamber temperatures ($17-20$ ℃) and water vapor concentration ($1.24-2.32$ g/m^3).
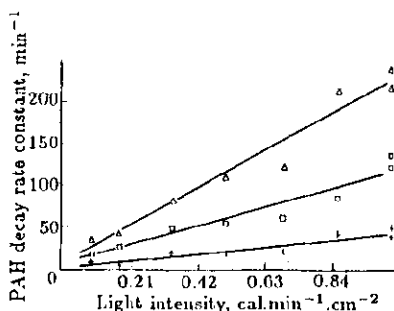

Fig.3 Correlation of PAH decay rate constant and light intensity

This plot suggests that there are a correlation between PAH decay rate constant K and light intensity I, which can be expressed as:

$$K = A \cdot I + B ,$$

where A and B are constants.

The exact mechanism about how light intensity affect PAH decay is not very clear. There exist several pathways for PAH decay, but recent experiments suggest that OH attack may be a significant one (Guo, 1987). It can be speculated that, when light intensity increased, the OH radical concentration will also be increased, then the chances for PAH and OH radical collision

will increase and PAH decay will be faster.

Fig. 4 suggests that there is a direct correlation between PAH decay rate constant K and water vapor concentration $[H_2O]$:

$$K = C \cdot [H_2O] + D.$$
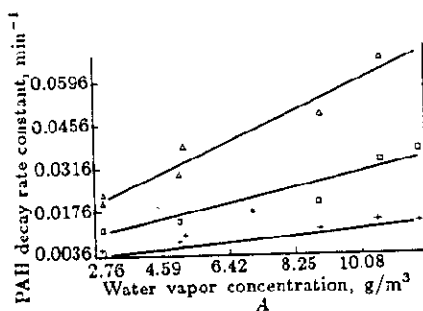
Fig. 4   Correlation of PAH decay rate constant and water vapor concentration
Temperature for these experiments ranged from 27 ℃ to 31 ℃ ;
the light intensity was 1.03 cal. min^{-1}.cm^{-2}

We assume that increase of water vapor concentration will result in increase of OH radical. As a result of OH radical increase, PAH decay will be faster.

Based on the similar reaction mechanisms of PAH with light and with water vapor, the correlation of PAH decay rate constant and light intensity should have similar mathematics form with that of PAH decay rate constant and water vapor concentration. This assumption has been supported by our experiments.

Temperature, PAH loading and PAH decay

A set of experiments had been carried out under different temperatures and approximate water vapor concentration ($1.03 - 3.17$ g/ m^3). The light intensity in these experiments was 1.03 cal. min^{-1}.cm^{-2}.

In Fig. 5, the natural logarithm of rate constant was plotted vs the inverse of the average absolute temperatures during the experiments, Arrhenius fit was observed between rate constant and temperature:

$$K = A \cdot \exp(-E/RT),$$

where A, E and R are constants.

From the data of Table 2, we can conclude that, PAH decay under low PAH loadings was faster than that under high PAH loadings when other factors are approximate.

It may be the reason that when PAH loading is high, there is no enough space on the particle surface to hold all of the compounds which include PAH, it suggests that a large part of
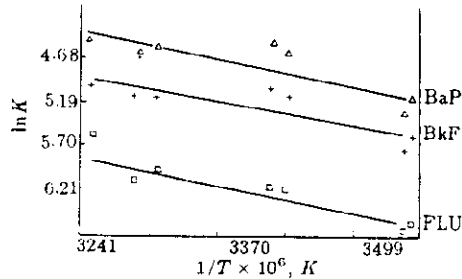
Fig. 5 Correlation of PAH decay rate constant and average temperature

PAH exist below the surface. If we assume that the rate of PAH diffuse to surface of particle is slower than the rate of surface reaction, the diffuse rate will dominate the process and limit the PAH loss. When PAH loading is low, surface reaction will be important and PAH will decay faster. In addition, competitive reaction on particle surface caused by other compounds may play an important role in the high PAH loading case and this will lower the reaction rate of PAH. This conclusion is consistent with the work of Kamens (Kamens, 1988).

Table 2   The influence of PAH loadings on PAH decay rate

Compound	Initial PAH loading, μg/g	Decay rate, min $^{-1}$
B(a)P	436	0.0121
	1607	0.0102
B(k)F	77	0.0079
	271	0.0068
FLU	427	0.0029
	1897	0.0022

The simulation of PAH decay in chamber

A multivariate regression analysis is carried out on the data of 19 individual coal soot experiments. The results suggest that there are direct correlation between decay rate constant (K) and sunlight intensity (I); water vapor concentration ($[H_2O]$) and absolute temperature (T). This correlation can be expressed as:

$$\ln K = A \cdot \ln I + B \cdot \ln[H_2O] + C/T + D,$$

another form of this formula is:

$$K(I, [H_2O], T) = E \cdot I \cdot [H_2O] \cdot \exp(-F/T),$$

where A, B, C, D, E and F are constants.

The results of regression analysis are listed in Table 3.

Table 3 The results of multiple regression analysis for the data of 19 experiments

| Compound | Parameter | | | | Correlation |
	A	B	C	D	coefficient
FLU	0.50	0.70	−5.8	−6.043	0.82
B(k)F	0.79	0.61	−18	−4.975	0.87
B(a)P	0.84	0.76	−1.5	−4.60	0.98

On the basis of conclusion obtained above, we developed a model to simulate the PAH decay in chamber. The model can be expressed by the formula:

$$Ct = C_0 \cdot \exp\left(-\int_0^t K\ (I,\ [H_2O],\ T)\ dt\right),$$

where the $K\ (I,\ [H_2O],\ T)$ can be substituted by the formula obtained above. C_0 is the initial concentration of PAH, Ct is the concentration of PAH after t minutes reaction.

The initial condition for this model has been assumed in Table 4 and Fig. 6.

Table 4 The parameter for the model

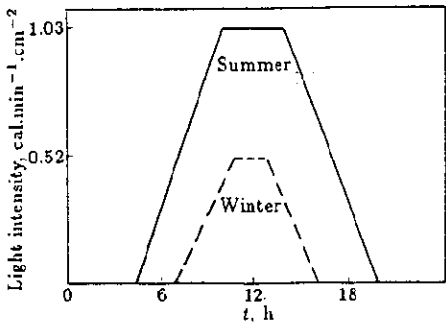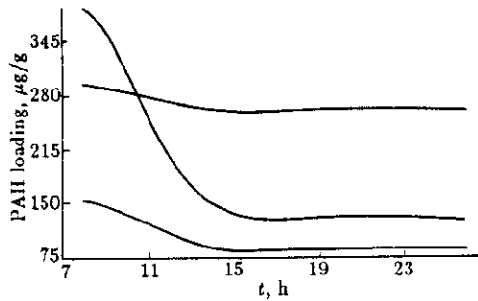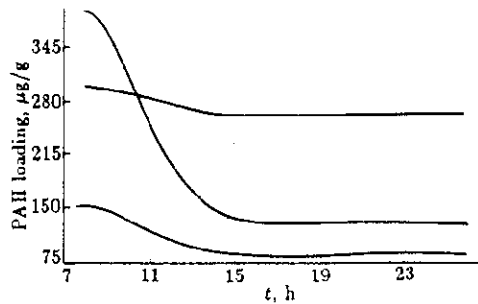| Season | Water vapor concentration, g/m³ | Temperature, ℃ | Initial PAH concentration, μg/g | | |
			B(a)P	FLU	B(k)F
Winter	1	0			
	1	−10	400	300	150
	2	0			
Summer	10	30	500	350	200

Fig. 6 Light intensity variation in a day in Beijing area
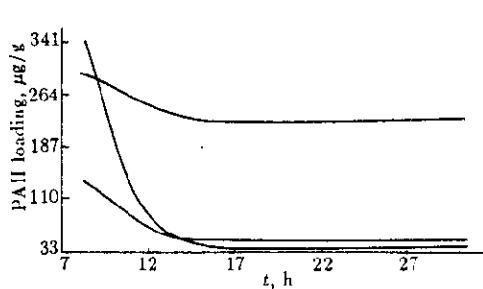
We can simulate the PAH loss behavior by using this model and PAH loss was plotted vs time in Fig. 7 to Fig. 10.

Fig. 7   Decay of PAH loading in Chinese coal soot in winter

   Temperature=0 ℃ ;   water vapor concentration =1 g/ m³

Fig.8   PAH decay on Chinese coal soot i Winter

   Temperature = −10 ℃ ;   water vapor concentration = 1 g/m³

Fig.9   PAH decay on Chinese coal soot in winter

   Temperature =0 ℃ ;   water vapor concentration =2 g/m³

The simulated PAH decay vs time course is consistent with our experiment results as well as the work of kamens *et al.* (Kamens, 1988).

It can be shown that the variance of environmental atmosphere temperature does not
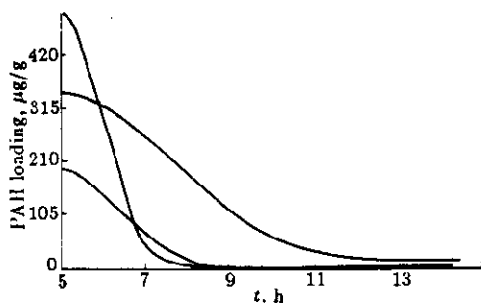
Fig. 10   PAH decay on Chinese coal soot in summer

Temperature = 30 ℃ ;   water vapor concentration = 10 g/m³

significantly affect the PAH decay by comparing the Fig. 7 and Fig. 8. We conclude that temperature is less important than sunlight intensity and water vapor concentration on PAH decay rate.

From Fig. 7 and Fig. 9, we observed water vapor concentration plays a very important role in PAH decay.

In Fig. 7 and Fig. 10, it is also found that PAH decay rate is very slow and some kinds of PAH can remain in air for several days in winter, but in summer the PAH decay rate constant is very large and it decomposes completely in several hours.

Two kinds of Chinese coal were used in our experiments. They were Datong coal and Mentougou coal. The PAH decay behavior of two kinds of coal soot is similar.

CONCLUSIONS

The photochemical reaction of PAH suggests first order reaction and a series of PAH decay rate constants are obtained for B(a)P, B(k)F and fluoranthene (FLU).

The correlation of some PAH decay rate constants and light intensity; water vapor concentration and temperature are obtained. The PAH decay rate constant is proportional to the light intensity and water vapor concentration. The influence of temperature can be interpreted by the Arrhenius formula.

A model about PAH loss has been set up and the simulating results agree with our experiments and the work of other researchers. We can conclude from the results that in winter PAH decay very slow and could be transported through long distance; but in summer, as the light intensity becomes stronger and the days are lengthening, the photolysis of coal particle PAH would be faster and their daytime half-lives are of the order of several hours.

PAH loading on coal soot particle have effect on PAH photolysis. When initial PAH loading is different significantly, higher loading means lower reaction rate under similar conditions.

The size distribution of coal soot particle changes very little during the course of reaction and the average size has a tendency to become smaller and this change has no observable influence on PAH decay.

REFERENCES

Guo, Z., Kamens, R. M. and Jeffries, H., Proceedings of the 1987 EPA/APCA Symposium on Measurement of Toxic Air Pollutants, Pittsburgh, PA, 1987, APCA VIP-8, EPA 600/9-87-010, 427

Kamens, R. M., Fulcher, J. M. and Guo, Z., Atmo

        R. M., Guo, Z., Fulcher, J. N. and Bell, D. A., Environ. Sci. Tech., 1988, 22(1): 103

Kamens, R. M., Perry, A. M,. Saucy, D. A., Bell, D. A., Newton, D. L. and Brand, B., Environ. Int., 1985b, 11: 131

Shabad, L. M., J. Natl. Cancer Inst., 1980, 64: 405