Disappearance of polycyclic aromatic hydrocarbons sorbed on surfaces of pine [*Pinua thunbergii*] needles under irradiation of sunlight: Volatilization and photolysis

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Abstract

The solar photodegradation of 16 polycyclic aromatic hydrocarbons (PAHs), sorbed on surfaces of pine [*Pinua thunbergii*] needles was investigated. The PAHs were produced by combustion of polystyrene and exposed onto the surfaces of pine needles. The disappearance of PAHs sorbed on the pine needle surfaces is mainly caused by volatilization and photolysis, with photolysis playing a major role. The volatilization rates correlate with PAH molecular weight significantly. The photolysis of the 16 PAHs follows first-order kinetics and their photolysis half-lives ($t_{1/2,P}$) range from 12.9 h for naphthalene to 65.4 h for fluorene. The PAHs have similar half-lives whether they are sorbed on spruce or pine needles. Compared with water, the cuticular waxes of pine needles can stabilize photolysis of PAHs and facilitate accumulation of PAHs. $t_{1/2,P}$ for selected PAHs correlate with semi-empirically calculated energy of the highest occupied orbital (E_{HOMO}). Photochemical behaviors of PAHs are dependent not only on their molecular structures but also the physical–chemical properties of the substrate on which they are adsorbed.
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Keywords: PAH; Pine needle; Photolysis; Solar irradiation

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are formed during combustion of fossil or biomass fuels, coal and oil refining. Many PAHs are carcinogenic and mutagenic, and some PAHs are endocrine disruptors (Vinggaard et al., 2000; Fertuck et al., 2001). PAHs constitute an important group of micro-pollutants, which can be found in different air, soil, water, vegetation, ice and sediment (Tremolada et al., 1996;

Holoubek et al., 2000; Buehler et al., 2001; Ghosh et al., 2003). It is difficult for most PAHs to undergo biodegradation (Cuypers et al., 2000). Photolysis is one of the major abiotic transformation processes for PAHs in the environment (Zepp and Schlotzhauer, 1979).

Photolysis rate of PAHs in aqueous phase was very fast, for which the half-lives ($t_{1/2}$) were only in a time scale of minutes or hours (Zepp and Schlotzhauer, 1979; Mill et al., 1981; Miller and Olejnik, 2001; Sabaté et al., 2001). Photolysis of PAHs in aqueous solutions may involve photoionization, self-sensitized oxidation by singlet oxygen and attack by hydroxyl radicals (Miller and Olejnik, 2001).

Quite a few researchers studied photochemical behavior of PAHs in particulate matters, such as fly ash, aerosol

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particulates, silica and carbon black (Behymer and Hites, 1985; Dabestani et al., 1995; Barbas et al., 1996, 1997; Pan et al., 1999; Reyes et al, 2000; Matsuzawa et al., 2001). It was found that photochemical behavior of PAHs is strongly dependent on the nature of the surface upon which the compound is sorbed (Korfmacher et al., 1980). The pathways of decay for PAHs sorbed on surfaces of atmospheric aerosol particles apparently depend on the aerosol organic composition of light-absorbing compounds present (McDow et al., 1994). Both hydrogen abstraction-initiated radical reactions and singlet oxygen attack are possible mechanisms of PAHs decomposition in atmospheric particulate matter (Jang and McDow, 1997). Generally, fly ash and carbon black can weaken or inhibit photolysis of PAHs and thus facilitate their transportation from combustion sources in the atmosphere (Behymer and Hites, 1985).

More than 80% of the Earth's land surface is covered with vegetation, and typically vegetation has a surface area that is 6–14 times greater than the land it covers (Simonich and Hites, 1994; Ockenden et al., 1998). Generally, the outer surfaces of vegetation are hydrophobic environments that can enrich hydrophobic organic pollutants mainly from atmosphere (Jensen et al., 1992; Keymeulen et al., 2001; Kylin et al., 2002; Hwang et al., 2003; Kylin and Sjodin, 2003). To facilitate understanding the fate of PAHs sorbed on surfaces of vegetation, it is of great importance to investigate their photochemical behavior on surfaces of leaves. Recently, Niu et al. (2003a, b) reported on photodegradation of PAHs and polychlorinated dibenzo-*p*-dioxin/furans (PCDD/Fs) sorbed on surfaces of spruce [*Picea abies* (L.) Karst.] needles. They found PAHs sorbed on spruce needles had longer $t_{1/2}$ values than in water.

Pine is one of the most widespread and typical vegetations in China. Although the photochemical behavior of PAHs on spruce needles has been investigated, it cannot be asserted whether PAHs sorbed on pine needles have same or similar photochemical behavior. It is thus the purpose of this study to investigate photochemical behavior of typical PAHs sorbed on surfaces of pine needles. In this study, needles of *Pinua thunbergii*, a widespread and typical pine species in Northeastern China, was selected as model vegetation. The pine needles were exposed to exhaust gas that contains PAHs produced by combustion of polystyrene, and then irradiated by sunlight.

2. Materials and methods

2.1. Materials

The 16 PAHs listed by US-EPA as priority pollutants (Callahan et al., 1979) were included in the current

study. HPLC grade hexane, acetone and dichloromethane were supplied by TEDIA (Fairfield, USA). An analytical standard solution of 16 EPA-PAHs ($100 \mu g \, mL^{-1}$, in cyclohexane) consisting of naphthalene (99.50%, Nap), acenaphthylene (99.50%, Acy), acenaphthene (99.50%, Ace), fluorene (98.50%, Fle), phenanthrene (98.90%, Phe), anthracene (99.50%, Ant), fluoranthene (98.00%, Fla), pyrene (99.50%, Pyr), benzo[*a*]anthracene (99.50%, BaA), chrysene (99.50%, Chr), benzo[*b*]fluoranthene (99.50%, BbF), benzo[*k*]fluoranthene (99.50%, BkF), benzo[*a*]pyrene (99.50%, BaP), dibenz[*a,h*]anthracene (98.50%, DaA), benzo[*g,h,i*]perylene (99.00%, BgP), and indeno[1,2,3-*cd*]pyrene (99.50%, IcP), together with deuterated internal standard ($2000 \mu g \, mL^{-1}$, in toluene), consisting of Nap (99.50%), Ace (99.50%), Phe (99.50%), Chr (99.50%), and perylene (99.50%), were obtained from Dr. Ehrenstoefer (Augsburg, Germany).

2.2. Photolysis experiment

Some 7-year-old pines [*P. thunbergii*] were placed in an exposure chamber and exposed to PAHs-containing exhaust produced by combustion of polystyrene in a designed combustion system that is similar to the one described by Niu et al. (2003a, b). About 3 kg of polystyrene was used for the combustion and the combustion process lasted for 2 h. After the combustion, the pines were kept in the exposure chamber for 48 h further to assure uniform distribution of PAHs on surfaces of pine needles.

The pines were exposed to full sunlight in Dalian (38°N, 121°E), Liaoning province, China, in September 2003 between 9.00 a.m. and 5.00 p.m. under clear sky conditions. The experiments were conducted over a 10-day period with a daily air temperature varying between 16.9 and 20.5 °C, average air pressure 1.009×10^5 Pa and relative humidity (70 ± 10)%. Some pines shielded from solar irradiation were used as dark controls, under the same atmospheric conditions. The purpose of the controls is to evaluate the other possible disappearance processes, such as evaporation and biological degradation. Periodically throughout the experiment, 20 g pine needles were collected for analysis, at the height of about 1 m, fully exposed to sunlight, as well as needles from the controls.

2.3. PAHs extraction

Every 5 g pine needles were extracted ultrasonically (KQ5200DB, Shumei, China) with 30 mL hexane/acetone (2:1, v/v) for 1 h and 400 ng deuterated PAHs as internal standard added prior to extraction. Then the samples were shaken for 1 h at 300 rpm by a constant temperature shaker to ensure intermixing and the extracts were concentrated to 1 mL by a rotary evaporator.

Using solid-phase extraction (SPE) method, PAHs were separated from interfering compounds in the extracts. The SPE treatment can purify the extraction and protect the chromatographic column in the subsequent GC–MS analysis. Meanwhile, it can reduce the interference peaks in the analysis proceeding. The SPE cartridges (65 mm × 13 mm I.D.) were made up of 2.0 g silica gel (100/200 mesh, activeness for 16 h at 130 °C) in lower part and 1.0 g anhydrous sodium sulfate (dryness for 16 h at 400 °C) in upper part. The cartridges were washed with 8 mL hexane immediately prior to use. The concentrated eluants were loaded onto the cartridges, which were then eluted with 8 mL hexane to leave the interfering compound on the column. Finally 8 mL hexane/dichloromethane (1:1, v/v) was added and the fraction containing PAHs was collected and further concentrated prior to GC–MS analysis.

2.4. Analytical method

Concentrations of PAHs were determined by a gas chromatography (Hewlett Packard GC 6890) equipped with a mass spectrogram (Hewlett Packard MS 5973N) and an auto-sampler (Hewlett Packard 7683). The capillary column used was HP-5MS, 30 m × 250 μm ID and 0.25 μm film thickness. The carrier gas was helium at a constant flow rate of 1.2 mL min^{-1}. The GC-oven was programmed to keep an initial temperature of 60 °C for 2.5 min followed by a heating rate of 40 °C min^{-1} up to 160 °C, then 5 °C min^{-1} up to 280 °C, held at 280 °C for 5 min, resulting in a total run time of 34 min. The mass detector operated in electron impact (70 ev), selected ion monitoring mode (SIM) and the m/z values as listed in Table 1.

Standard curves were obtained using 50, 100, 200, 400, 700, 900 ng mL^{-1} PAH standards. Internal standardization was used for quantification by employing the five internal standards at 400 ng mL^{-1}. The response curves for 16 PAHs were linear and the correlation coefficients were more than 0.993. Fig. 1 presents GC–MS chromatograms for the mixture of the standards.

2.5. UV–visible absorption spectrum of wax and lipid

To determine UV–visible absorption spectra of the wax and lipid extracted from the pine needle surfaces, 5 g pine needles was extracted by 20 mL hexane for 2 h in an ultrasonic bath and then the solution was passed over anhydrous sodium sulfate to remove water. Using a 10 mm quartz cell and hexane as reference, the UV–visible absorption spectrum of the solution was determined by a diode array spectrophotometer (Jasco, Japan).

3. Results and discussion

3.1. Kinetics

The decreases of PAHs are shown in Fig. 2, for naphthalene (low molecular weight), pyrene (medium molecular weight) and indeno[1,2,3-cd]pyrene (high

Table 1

Retention time, quantification ion and conformation ion of the 16 EPA PAHs and 5 D-PAHs internal standards

| No.	PAH compounds	Retention time (min)	Quantification ion	Confirmation ion
1	[²H₁₀]Naphthalene	5.663	136	134, 137
2	Naphthalene	5.681	128	127, 129
3	[²H₁₀]Acenaphthene	7.508	164	162
4	Acenaphthylene	7.761	152	150, 153
5	Acenaphthene	7.814	154	152, 153
6	Fluorene	8.782	202	101, 200
7	[²H₁₀]Phenanthene	11.179	188	187, 189
8	Phenanthene	11.249	178	176
9	Anthracene	11.385	178	176
10	Fluoranthene	15.456	202	101, 200
11	Pyrene	16.286	202	101, 200
12	[²H₁₂]Chrysene	21.592	240	236
13	Benzo[a]anthracene	21.531	228	114, 226
14	Chrysene	21.696	228	114, 226
15	Benzo[b]fluoranthene	26.128	252	125, 250
16	Benzo[k]fluoranthene	26.224	252	125, 250
17	Benzo[a]pyrene	27.334	252	125, 250
18	[²H₁₂]Perylene	27.573	264	—
19	Indeno[1,2,3-cd]pyrene	31.813	276	138, 277
20	Dibenz[a,h]anthracene	32.056	278	276, 279
21	Benzo[g,h,i]perylene	32.950	276	138, 277
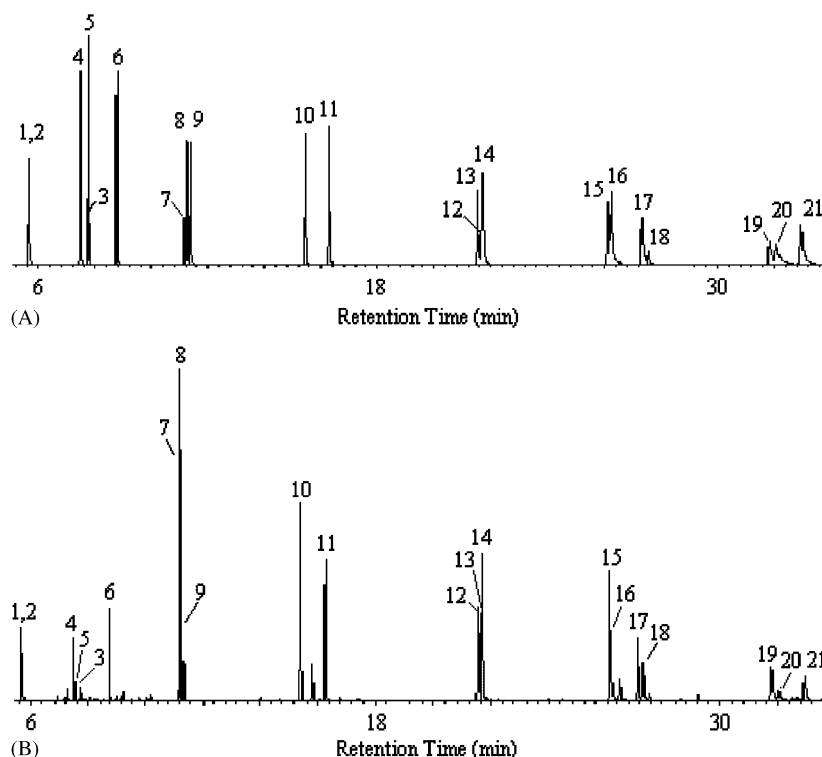
Fig. 1. The selected ion chromatograms of the 16 standard PAHs and 5 D-PAH internal standards (A) and the photolysis samples (B). The numbers correspond to those in Table 1.

molecular weight) as examples. It reveals that the non-photochemical disappearance of PAHs in the controls cannot be neglected. Assuming that the disappearance of PAHs in the dark controls follows the first-order kinetics, disappearance rate constants of PAHs in the control experiments (k_C) were calculated, which are listed in Table 2. Non-photochemical disappearance may include volatilization and biological degradation, but biodegradation of PAHs is difficult in 10 days (Chainsaw et al., 1995). Thus, volatilization may have a dominative effect on the decrease of PAHs in dark control experiments. Fig. 3 shows a linear correlation between molecular weight (Mw) of PAHs and their half-lives in the controls ($t_{1/2,C}$). Previous studies indicated that PAHs with high Mw tend to have low vapor pressures (Huang et al., 2004). Thus it is reasonable that high Mw PAHs have low k_C and high $t_{1/2,C}$ values. The current k_C values are generally higher than the corresponding k_C values determined by Niu et al. (2003a) who used spruce [*Picea abies* (L.) Karst.] needles as model vegetation. The k_C values depend on the nature of the surfaces on which PAHs sorbed and all kinds of weather conditions, such as the wind speed, temperature and air pressures. One possible reason that may lead to the higher k_C values in the current study is the evidently larger wind speed in Dalian than Munich.
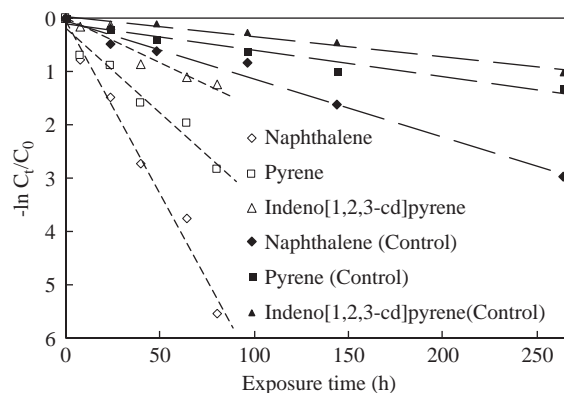

Fig. 2. The decrease of selected PAHs in sunlight irradiation and dark control experiments. C_t is the concentration of each PAH at time t and C_0 is the initial concentration.

It can be observed from Fig. 2 that the plots of $-\ln(C_t/C_0)$ versus time for selected PAHs are linear. It is thus reasonable to use pseudo-first-order kinetics in deriving the total disappearance rate constants (k_T) of PAHs. In the process of the photolysis experiment, both photochemical degradation and non-photochemical disappearance may occur on the surfaces of pine needles.

Table 2
The kinetic parameters for the decay of PAHs

PAH	k_T (h^{-1})	R^2	$t_{1/2}$(h) Total	k_C (h^{-1})	R^2	$t_{1/2}$(h) Control	k_P (h^{-1})	$t_{1/2}$ (h) Photolysis
Nap	0.0646	0.984	10.7	0.0109	0.981	63.6	0.0537	12.9
Acy	0.0250	0.913	27.7	0.0090	0.902	77.0	0.0160	43.3
Ace	0.0210	0.973	33.0	0.0084	0.876	82.5	0.0126	55.0
Fle	0.0174	0.884	39.8	0.0068	0.861	101.9	0.0106	65.4
Phe	0.0201	0.856	34.5	0.0065	0.898	106.6	0.0136	51.0
Ant	0.0310	0.903	22.4	0.0072	0.986	96.3	0.0238	29.1
Fla	0.0322	0.962	21.5	0.0051	0.947	135.9	0.0271	25.6
Pyr	0.0316	0.963	21.9	0.0050	0.957	138.6	0.0266	26.1
BaA	0.0336	0.990	20.6	0.0045	0.946	154.0	0.0291	23.8
Chr	0.0257	0.912	27.0	0.0031	0.929	223.5	0.0226	30.7
BbF	0.0184	0.869	37.7	0.0033	0.907	210.0	0.0151	45.9
BkF	0.0245	0.947	28.3	0.0038	0.926	182.4	0.0207	33.5
BaP	0.0207	0.888	33.5	0.0035	0.947	198.0	0.0172	40.3
IcP	0.0168	0.919	41.3	0.0038	0.967	182.4	0.0130	53.3
DaA	0.0187	0.936	37.1	0.0038	0.907	182.4	0.0149	46.5
BgP	0.0157	0.858	44.1	0.0034	0.939	203.8	0.0123	56.3
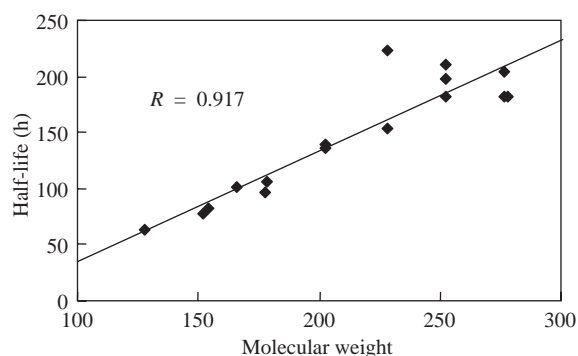
Fig. 3. The increase of half-lives in dark controls with the increase of molecular weight of PAHs.
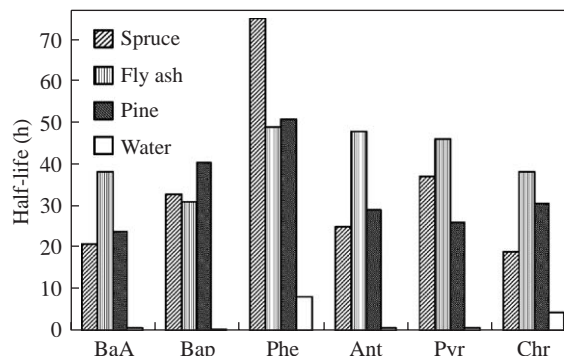

Fig. 4. Comparison of the photolysis half-lives in natural water with these on the surfaces of pine needles, spruce needles and fly ash for selected PAHs.

The photolysis rate constant (k_P) can be obtained by subtracting k_C from k_T. These rate constant values and their corresponding half-life values are listed in Table 2. As k_P is far greater than k_C, it can be concluded that photodegradation play an important role on the fate of PAHs sorbed on surfaces of pine needles under irradiation of sunlight.

3.2. Factors affecting photolysis rates

Photolysis half-lives of selected PAHs dissolved in water (Zepp and Schlotzhauer, 1979), sorbed on fly ashes (Behymer and Hites, 1985), waxes of spruce needles ($t_{1/2,S}$) and pine needles ($t_{1/2,P}$) are summarized in Fig. 4. The half-lives in water ($t_{1/2,W}$) are far lower than the corresponding values for PAHs sorbed on other

environmental media. For example, $t_{1/2,W}$ of benzo[a]-pyrene is 0.54 h, in contrast, the corresponding $t_{1/2,P}$ is 40.3 h. These data further demonstrate that photolysis rates of PAHs are much faster in natural water body than in the waxes of pine needles. The result indicates that PAHs on the surfaces of pine and spruce needles by dry and wet deposition would be stable and accumulate to reach a certain concentration.

The present $t_{1/2,P}$ values are compared with those determined on surfaces of spruce needles (Niu et al., 2003a) in Fig. 5. The correlation coefficient between the two sets of half-lives is 0.857 ($p < 0.001$). Statistical paired t-test (Montgomery and Runger, 2003) was performed to verify whether the values of $t_{1/2,S}$ and $t_{1/2,P}$ have significant differences. The null hypothesis is that there is no difference between $t_{1/2,S}$ and $t_{1/2,P}$, H_0: $t_{1/2,S} = t_{1/2,P}$. By K–S one-sample test that verify
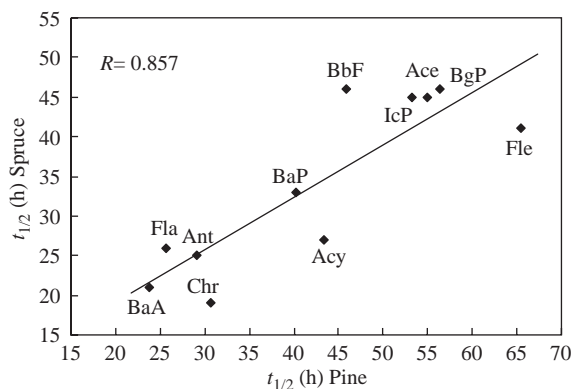
Fig. 5. Comparison of the photolysis half-lives on spruce needles surfaces with these in the waxes of pine needles for selected PAHs.
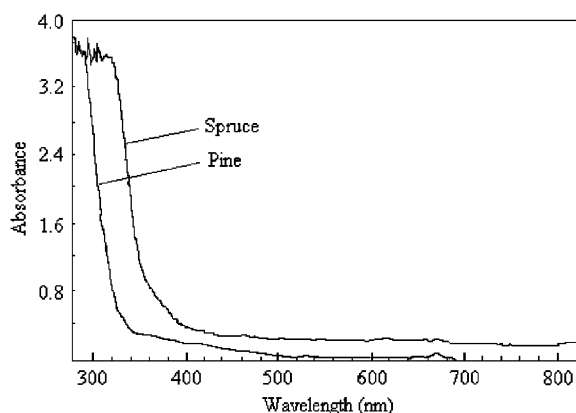

Fig. 6. UV–visible absorption spectrum of the wax and lipid extracted from pine needles and spruce needles.

whether a population is normally distributed (Montgomery and Runger, 2003), it was found both $t_{1/2,S}$ and $t_{1/2,P}$ are normally distributed. The t-test statistic was calculated to be $t = 1.494$. The sample number $n = 15$, thus at 0.05 level of significance level (p), critical value of t-test is 2.144. As $|t| < 2.144$, the null hypothesis, H_0, cannot be rejected at $p = 0.05$. That is, there is no strong evidence to conclude that $t_{1/2,S}$ differs from $t_{1/2,P}$. Thus, PAHs exhibit similar photolysis rates on the surfaces of spruce needles and pine needles.

It needs to be mentioned that the sunlight irradiation intensity in the experiment of Niu et al. (2003a), $620 \pm 50 \, \text{W} \, \text{m}^{-2}$, is stronger than in the current study, $450 \pm 50 \, \text{W} \, \text{m}^{-2}$. In addition, the waxes of pine needles have relatively weak light absorption for 300–400 nm band compared with spruce needles (Fig. 6). The similar photolysis rates between the two kinds of needles suggest that the waxes in the pine and spruce needles play a light filtering effect, with the light filtering effects

of spruce needles being stronger than pine needles. Thus although the light intensity of the current study is weaker than in the previous study (Niu et al., 2003a), the weaker light absorbance in 300–400 nm band for waxes of pine needles than spruce needles leads to relatively larger light penetration depth in surfaces of pine needles than spruce needles, resulting in comparable photolysis rates between the two kinds of needles.

Generally, the more polar the solvent, the faster the photodegradation of PAHs (Lehto et al., 2000). This solvent-specific phenomenon is related to the photolysis mechanism of PAHs. There are two main initial pathways of PAHs' degradation: direct photolysis (photoionization or photohydrolysis) or indirect photolysis (photosensitization reaction or self-sensitized oxidation by singlet oxygen). After absorbing photons, PAH molecules are excited. The excited PAHs can return to the ground state dissipating energy in various ways. One is that photo-excited PAHs can undergo chemical reactions, for example, electron or proton transformation. In aqueous solution, the most probable is the electron transfer between excited PAHs and dissolved oxygen and water (Fasnacht and Blough, 2002). As a result of electron transfer, PAHs cation radicals and superoxide anions can be formed. The resultant PAHs cation radicals can polymerize on dry surfaces (Dabestani et al., 1995) or react with water or hydroxide ion to form the secondary intermediates, which can react further to form stable products. The other is that photoexcitation PAHs can engage in energy transfer to oxygen with a subsequent singlet state oxygen formation. Singlet oxygen, a moderate oxidant, can attack molecular PAHs in the ground state through addition to aromatic systems (Sigman et al, 1998; Kong and Ferry, 2003). In highly polar media, such as water, the charge transfer state would be further stabilized, possibly to give solvent separated ionic species, and additional chemistries could arise from a PAH radical cation and superoxide (Sigman et al., 1998). Moreover, singlet oxygen has longer life in polar solvent, for example, $30 \, \mu\text{s}$ in acetonitrile and $7 \, \mu\text{s}$ in methanol (Wasserman and Murray, 1979), easily to initiate photooxidation of PAHs. The waxes of pine needles consist mainly of long-chain esters, polyesters and paraffins (Kylin et al., 1994), for which the polarity is weaker than water. In addition, these materials can act as quenchers of singlet oxygen. PAHs can also react with hydroxyl radical generated by superoxide reaction with water after absorbing photo in aqueous solvent (Miller and Olejnik, 2001). It is thus reasonable that photolysis rates for PAHs are much faster in water than in waxes of the pine needles.

Compared with PAHs dissolved in water, the high photolysis half-lives of PAHs sorbed on fly ash, spruce needles, or pine needles, suggest the waxes of pine and spruce needles as well as fly ash can stabilize photolysis of PAHs. The PAHs studied here have absorption bands
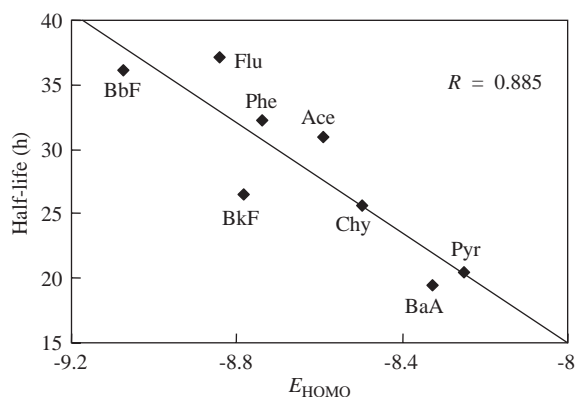
Fig. 7. The relationship between $t_{1/2,P}$ of selected PAHs and E_{HOMO}

in wavelength range 230–410 nm (Matsuzawa et al., 2001; Miller and Olejnik, 2001) and the waxes of pine needles have the strong absorption in 200–320 nm region (Fig. 6). As the waxes can stabilize photolysis of PAHs by acting as filters of the incident light, only PAHs present on the surfaces of the pine needles are accessible to the sunlight, making photolysis possible.

Behymer and Hites (1985) studied photolysis of 15 PAHs adsorbed on silica gel, alumina, fly ash, and carbon black. They found the observed half-lives of some PAHs adsorbed on silica gel can be explained by structure–property relationships using Dewar reactivity numbers. For the current study, structure–property relationship (Fig. 7) can also be obtained for 8 PAHs between $t_{1/2,P}$ and energy of the highest occupied molecular orbital (E_{HOMO}) that was calculated using PM3 semi-empirical method of MOPAC (2000) contained in the CS Chem3D Ultra (Ver. 6.0, Cambridge-Soft.com). It indicates that $t_{1/2,P}$ decrease with the increase of E_{HOMO} for the PAHs. A similar conclusion was drawn by Chen et al. (2000) who studies quantitative structure–property relationships (QSPR) for PAHs photolysis in water body. As E_{HOMO} characterizes the ability of a molecular to lose electrons, and compounds with high E_{HOMO} tend to lose electrons easily, the QSPRs support the aforementioned photolysis mechanism of PAHs, photo-oxidation. However not all PAHs under study follow the relationship indicated by Fig. 7, which implies not only molecular structures governs $t_{1/2,P}$, but also the characters of pine needles on which PAHs are adsorbed play a major role on photodegradation of PAHs, like silical gel.

4. Conclusions

The disappearance of PAHs sorbed on the pine needles surfaces is mainly caused by volatilization and photolysis. Volatilization rates correlate with PAH molecular weight significantly. Photolysis rates are much faster than volatilization rates, suggesting that photolysis play a major role in the fate of PAHs sorbed on the pine needles surfaces. The photolysis of the 16 PAHs follows first-order kinetics and $t_{1/2,P}$ range from 12.9 h for naphthalene to 65.4 h for fluorene. The PAHs have similar half-lives whether they are sorbed on spruce or pine needles. Compared with water, the cuticular waxes of pine needles can stabilize photolysis of PAHs and facilitate accumulation of PAHs. $t_{1/2,P}$ for selected PAHs is correlated to the semi-empirically calculated E_{HOMO}. Photochemical behaviors of PAHs are dependent not only on their molecular structure but also the physical and chemical properties of the substrate on which they are adsorbed.

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