

In Situ Monitoring the Photolysis of Fluoranthene Adsorbed on Mangrove Leaves Using Fiber-Optic Fluorimetry

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Abstract A newly established fiber-optic fluorimetry was used to determine the fluoranthene (Fla) adsorbed on the leaf surfaces of three mangrove species, such as *Excoecaria agallocha* (*Ea*), *Kandelia candel* (*Kc*) and *Aegiceras corniculatum* (*Ac*). With the method, the photolysis of Fla adsorbed on *Ea*, *Kc* and *Ac* leaf surfaces was studied. Under the laboratory conditions, using a high pressure mercury lamp as light source, photolysis was found to be the main transformation pathway for the Fla adsorbed on the three mangrove leaves, whereas disappearance of the adsorbed Fla as a result of volatilization and absorption could be negligible. The photolysis of Fla adsorbed on the three mangrove leaf surfaces followed first-order kinetics with photolysis rates of Fla in the order of $Ac > Ea > Kc$. The photolysis half lives of Fla adsorbed on the leaves were from 14.32 min to 69.31 min. The different initial concentrations of Fla adsorbed on the selected mangrove leaves did not affect the photolysis rates of Fla. The absorption characteristics of leaf-wax played an important role to influence the different photolysis rates of Fla adsorbed on these three mangrove species.

Keywords Fiber-optic fluorimetry · In situ · Photolysis · Fluoranthene · Mangrove leaf surface

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are considered as highly bioaccumulated persistent organic pollutants, which can be widely found in the atmosphere, water, vegetation, ice, sediment and soil [1, 2]. Recently, they have become one of the hottest research fields in environmental science because of their potential carcinogenicity, mutagenicity and teratogenicity to aquatic organisms and human [3, 4]. Most PAHs, especially with four or more rings, are difficult to be biodegraded in the environment because of their poor water-solubility [5]. However, some researches showed that most PAHs in the environment have photo-induced toxicity [6, 7], and that the delocalized π bond of PAHs can absorb the visible and ultraviolet parts of sunlight [8]. Therefore, photolysis is recognized as an important transformation pathway for PAHs in the environment, and has being attracted great attention [9, 10].

More than 80% of the land surface on earth is covered with vegetation, and typically vegetation has a leaf surface area that is 6–14 times greater than the land it covers [11]. Furthermore, leaf surfaces are covered with a complex lipid cuticle that can adsorb hydrophobic organic pollutants from the atmosphere. As a result, it is generally believed that the adsorption of PAHs by leaves is the most important pathway by which they become enriched in vegetations [12, 13]. And some researches have shown that the larger surface area and more leaf-wax content a leaf is the more PAHs it can adsorb [12, 14, 15].

The mangrove ecosystem, as a special ecological landscape with its unique features of high primary productivity, abundant detritus, rich organic carbon and anoxic conditions,

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is reported as an important site to absorb and accumulate pollutants such as PAHs from anthropogenic and natural sources in coastal areas. It is also a crucial habitat for marine and estuary organisms to live in, since this is where the main source of food is provided for them [16]. Most of mangrove leaves, in order to adapt to their special ecological habit, are common with large surface areas and thick lipid cuticle. Simonich and his co-workers have developed a mass-balance model for measuring the amount of the PAHs from the atmosphere, and their results showed that 22–62% of the PAHs emitted into the atmosphere were removed by plant leaves in the northeast of the United States [17]. However, after the adsorption of PAHs by mangrove leaves, the roles of mangrove leaves on the environmental behaviors of PAHs adsorbed on them, for instance, where the PAHs adsorbed on the mangrove leaves gone, what is the main transformation pathway of PAHs adsorbed on the leaf surface including photolysis, volatilization and leaf absorption, were unknown. These questions are greatly significant for us to know more the environmental fate of PAHs adsorbed on mangrove leaves.

Since now, notable progress has been made on studying the photolysis of PAHs in liquid medium or adsorbed on particles [10, 18–23], but little work has been reported on the photolysis of PAHs adsorbed on mangrove leaf surfaces. Some researchers reported the photolysis of PAHs adsorbed on spruce or pine needles, and their results showed that photolysis of some PAHs on spruce or pine needles might play an important role in the environmental fate of PAHs [24–26]. Here, *Ea*, *Kc* and *Ac*, three of the most widespread mangrove species in China were selected and used in the following experiment. Obviously, the leaf morphology of *Ea*, *Kc* and *Ac* are quite different from spruce and pine needles, hence, the results they obtained whether would be suitable to mangrove leaves or not is still unknown. On the other hand, the traditional methods utilizing the entirely destructive chemical extraction techniques might destroy the originally existing forms and eliminate the spatial distribution of PAHs in/on the leaves. Furthermore, the methods, which were used in the published works, needed an extraction separation before sample analysis. This is not only time/labor consuming, but also causes secondary pollution problems because of the organic solvent used. It is evident that these methods can not be used directly for in situ monitoring of PAHs adsorbed on leaves.

In this work, Fla with a high fluorescence quantum yield, was selected as a model PAH compound. A high pressure mercury lamp, which emits both ultraviolet and visible light, was used as the light source to carry out the photolysis experiment. Because optical fiber has many advantages, such as high light focalization, low weight and small size, which make it suitable for on-line, in situ and remote detection of pollutants [27–33]. Therefore, a fiber-optic fluorimetry was employed to in situ investigate the

photolysis processes of Fla adsorbed on the three mangrove leaves under the laboratory experimental conditions.

Materials and Methods

Sample Collection

Mangrove hypocotyls of *Kc* and *Ac* were collected from Longhai mangrove reserve located in Zhangzhou, Fujian, China (east longitude: 117°29′–118°14′; north latitude: 24° 11′–24°36′; altitude: 0 m above sea level). *Kc* and *Ac* hypocotyls of about the same size and maturity were sampled and quickly taken to laboratory for cultivation. *Ac* and *Kc* leaves were collected from these mangrove seedlings cultivated for about 18 months. *Ea* hypocotyls were sampled from Hong Kong and have been cultivated for about 20 months before *Ea* leaves were collected for the experiment. After the collection of mangrove leaves, experiments were carried out as soon as possible.

Preparation of Fla-Acetone Solution

Fla (Aldrich, USA, purity > 99%) stock solution was prepared by dissolving 0.0100 g Fla in 100 mL acetone in a brown volumetric flask, which was stored at 4°C in darkness to avoid possible photodegradation. Working solutions of Fla were prepared by diluting the stock solution with acetone just prior to be used.

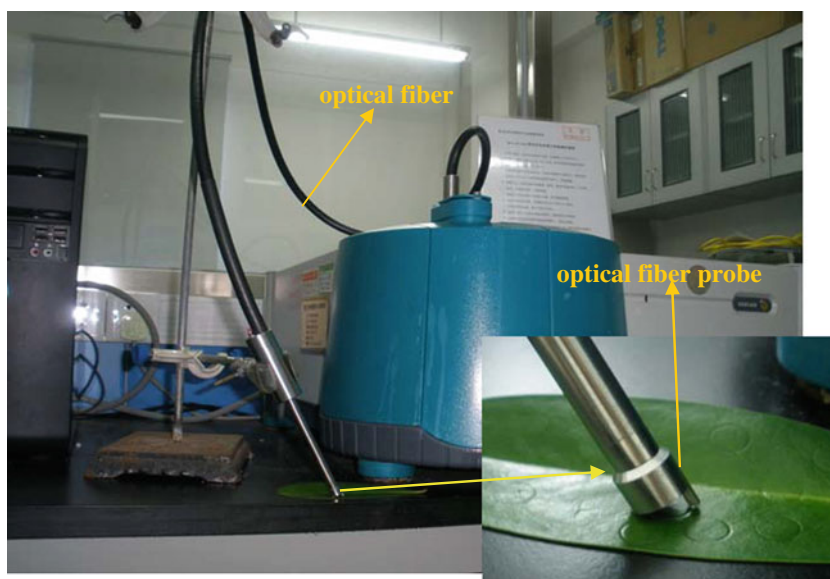
Pretreatment of Mangrove Leaves for the Experiment

The picked fresh mangrove leaves were carefully rinsed with tap water and Milli-Q water three times respectively before use. After air-drying, the large circle end of a 5 mL pipette was employed to lightly press circles on the surfaces of mangrove leaves. The area of each circle is about 0.28 cm², and it was defined as a unit of ‘spot’ which had a same size as the fiber optical probe. Then Fla-acetone working solutions were introduced onto these ‘spots’ using a 10 µL flat head micro-injector at room temperature.

Determination of Fla Adsorbed on Mangrove Leaves

After volatilization of the acetone naturally from the ‘spots’ on the mangrove leaves at room temperature, the marked ‘Fla spot’ on the mangrove leaves were placed under the fluorescence optical fiber probe. After a certain interval, the relative fluorescence intensities of ‘Fla spot’ adsorbed on the leaves were directly determined by a Cary Eclipse fluorescence spectrophotometer equipped with a 150-W Xenon flash lamp and fiber optic accessories (Varian, USA). Instrumental parameters were as follows: excitation

Fig. 1 Determination device for the Fla adsorbed on leaf surface of *Kc*



and emission slits were set at 20 and 10 nm; scan speed was 600 nm min^{-1} ; PMT voltage was 600 V. An angle between the fluorescence spectrophotometer fiber-optic probe and the tested mangrove leaves was kept at 45° throughout the experiments to avoid the interference from the scattered light (Fig. 1). With the advanced read model of Cary Eclipse software for acquiring and processing the spectral data, with optimized excitation and emission wavelength of Fla adsorbed on different mangrove leaves, each sample can be determined not more than 1 min. Three leaves of each species with about the same background values were selected, and the detection areas were selected at the front, middle and nether parts of the leaves as showed in our previous study [34]. Average values for nine times determination of each 'spots' were used in the final results, and the relative standard deviations ($n=9$) were also calculated.

Photolysis of Fla Adsorbed on Mangrove Leaves

The photolysis processes of Fla adsorbed on the three mangrove leaves were investigated by using a high pressure mercury lamp as the light source (including optical fiber) (CHF-XM500 W, Beijing Trusttech, Co., Ltd., China). In order to keep the emit light intensity steady during the experiment, the mercury lamp must be preheated for half an hour before starting the experiment. The light intensity on the leaf surfaces was controlled by adjusting the height between the mangrove leaf surfaces and the optical fiber probe of the mercury lamp. The proper illumination intensity on the leaf surfaces was controlled at $8.62(\pm 0.07) \times 10^4 \text{ lx}$, which was determined by a ZDS-10 illuminometer (Shanghai, China), in the photolysis experiments. The temperature and relative humidity during the photolysis experiment were $25 \pm 0.2^\circ\text{C}$ and $58 \pm 4.0\%$, respectively. Leaves with Fla adsorbed on

them were put under the mercury lamp whose light is guided by an optical fiber to avoid heating effects on the photolysis processes caused by the mercury lamp after a certain period of illumination. The relative fluorescence intensities of Fla adsorbed on mangrove leaves were detected by using the fiber-optic fluorimetry. Volatilization and absorption of the Fla adsorbed on the leaves should be investigated to explain the disappearance of the Fla adsorbed on the leaf surfaces. Therefore, control experiments were carried out involving to keep the leaves in darkness, and the relative fluorescence intensities of Fla was determined with a same time interval during the photolysis experiments.

UV-vis Spectrum of Fla Dissolved in Water

UV-vis spectra, which can show the exact absorption characteristic of the target compounds, are very important

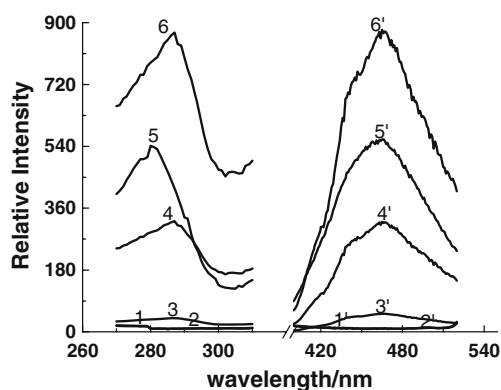


Fig. 2 The fluorescence excitation and emission spectra of Fla adsorbed on *Kc* leaves ($\lambda_{em}=466.06 \text{ nm}$, $\lambda_{ex}=286.00 \text{ nm}$), 1.1': blank; 2.2': blank+acetone; 3.3': 15 ng/spot Fla; 4.4': 400 ng/spot Fla; 5.5': 0.1 mg/L Fla in Milli-Q water; 6.6': 1000 ng/spot Fla

Table 1 The analytical characteristics of the method

Mangrove	Calibration curve	Linear range(ng/spot)	Correlation coefficient	Detection limit ^c (ng/spot)
<i>Kc</i>	$y^b=1.409x^a+28.3$	1.0–620	0.9853	0.80
<i>Ea</i>	$y=1.040x+16.0$	2.5–680	0.9991	1.45
<i>Ac</i>	$y=0.688x+13.5$	10–710	0.9881	3.01

^a stands for the concentration of Fla added to the surface of mangrove leaves

^b stands for the fluorescence intensity of Fla adsorbed on the surfaces of mangrove leaves

^c stands for the detection limit of the method, which was calculated by $3Sb/K$, where Sb stands for the standard deviation of the blank ($n=9$), K stands for the slope of calibration curves

for explaining the different photolysis results [24–26]. As for better understanding whether Fla adsorbed on mangrove leaves can be photodegraded or not under the illumination of mercury lamp, the UV–vis spectrum of Fla should be obtained. 40 μ L of 50 mg/L Fla-acetone solution was transferred into a colorimetric tube. Milli-Q water was added to the mark after the evaporation of the solvent by a gentle flow of high-purity nitrogen gas ($\geq 99.9\%$). To ensure the sufficiently dissolved of Fla, the tube with Fla was ultrasonicated (KQ-3200, Kunshan Ultrasonic Instrument Co., Ltd., China) for 30 min at room temperature and then kept in dark for 5 h, as well as to avoid possible photolysis. Finally, the UV–vis spectrum of Fla was obtained by a UV–vis Spectrophotometer (Varian, USA). This experiment was repeated three times.

Statistical Analysis

In this work, measurements of Fla adsorbed on mangrove leaves and the photolysis experiments were all performed for 9 times, and the average means was used to express the final results. Statistical analysis for the variation of the fluorescence intensity obtained was performed using the statistics package for social science (SPSS) 13.0 for Windows. The significant differences in the results were

determined using a one-sample *t*-test at the 95% confidence level ($p < 0.05$ means that a remarkable difference existed).

Results and Discussion

Fluorescence Excitation and Emission Spectra of Fla Adsorbed on Mangrove Leaves

As mentioned above, the excitation and emission wavelengths for determination of Fla adsorbed on each kind of mangrove leaf were optimized, which were as follows ($\lambda_{ex}/\lambda_{em}$): *Kc* 286.00/466.06 nm, *Ea* 280.00/465.07 nm and *Ac* 285.00/466.06 nm, respectively. In order to make sure that the autofluorescence of each mangrove leaf would not interfere with the determination of Fla, the fluorescence spectra of uncontaminated leaves, acetone as a blank, different concentrations of Fla adsorbed on leaves, as well as the fluorescence spectrum of 0.1 mg/L Fla aqueous solution were scanned by the established method. Results were shown in Fig. 2. From Fig. 2, we found that the autofluorescence intensity of the uncontaminated *Kc* leaves was less than 20, and the acetone used as blank had little influence on the blank values of *Kc* leaves. These results illustrated that both of them showed no interference to the measurement of Fla adsorbed on the leaves. Compared to the fluorescence spectra obtained from Fla aqueous solu-

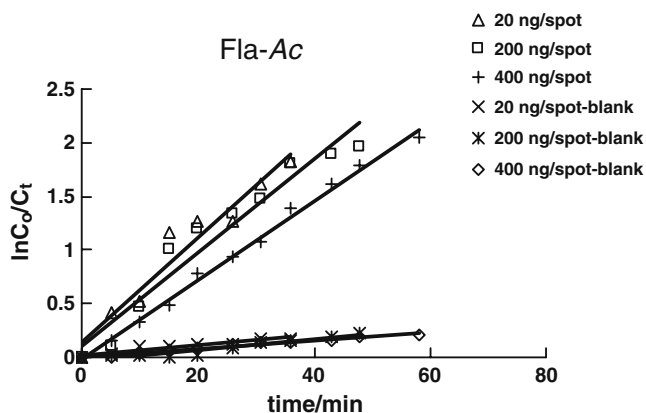


Fig. 3 The photolysis kinetics of different initial concentrations of Fla adsorbed on the upper surfaces of *Ac* leaves ($n=9$)

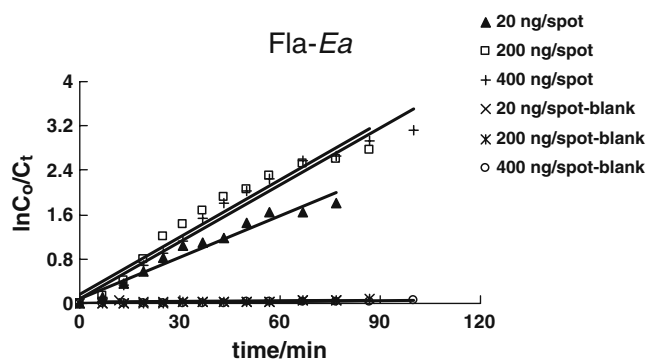


Fig. 4 The photolysis kinetics of different initial concentrations of Fla adsorbed on the upper surfaces of *Ea* leaves ($n=9$)

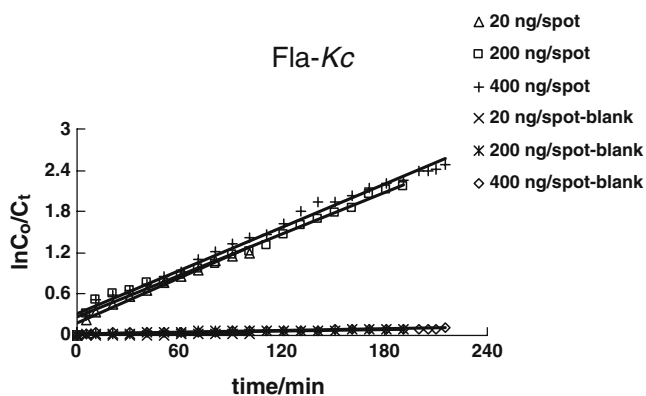


Fig. 5 The photolysis kinetics of different initial concentrations of Fla adsorbed on the upper surfaces of *Kc* leaves ($n=9$)

tion, there were no obvious changes either in intensity or shapes of the fluorescence emission spectra, but a slight red-shift had happened to the excitation spectra. This may be due to the different polarities of the matrices in which Fla was adsorbed. Similar results were observed for Fla adsorbed on the leaves of *Ea* and *Ac* (results were not shown here). All of the above results demonstrated that fiber-optic fluorimetry was acceptable to be used as an in situ method for the determination of Fla adsorbed on mangrove leaves.

Analytical Merits of the Established Method

Since the amount of PAHs adsorbed on plant leaves were very small in the environment, therefore, accurately quantifying the amount of Fla adsorbed on plant leaves is a prerequisite for the following photolysis experiments. Therefore, different concentrations of Fla-acetone solution were prepared and spotted onto the tested mangrove leaves, and the relative fluorescence intensities from each spot were detected. The results revealed that the concentration of Fla in a certain range showed a good linear relationship with their relative fluorescence intensities, but with different detection limits. The experimental results were shown in Table 1. From Table 1, it can be seen that the linear dynamic ranges

and detection limits were a little different from our previous work [29], and with a relative standard deviation less than 3.71%. The reason was that the mangrove leaves used in this paper were different from mangrove seedlings cultivated by ourselves. The fluorescence intensities of the same amount of Fla adsorbed on the different matrices would be different [12]. During the experiment, it was found that mangrove leaves cultivated by ourselves were thicker than those from field collection. Since different growth conditions would certainly change the ecological characteristics of mangrove leaves.

Recovery Experiment

To carry out the investigation of the photolysis processes, it is very necessary to make sure that the method used was accurate enough for the determination of the Fla adsorbed on leaves. Therefore, a recovery experiment was carried out as previously reported [27–29]. The recovery experimental results for Fla adsorbed on *Ea*, *Kc* and *Ac* leaves were 72.9–113.3, 89.8–119.2 and 88.7–98.9%, respectively.

Photolysis of Fla adsorbed on the upper leaf surfaces of mangrove leaves.

Results of the Photolysis Experiments

It has been reported that the ‘sun’ leaves (the upper leaf surface) have thicker epicuticular wax layers than ‘shade’ leaves (the lower surface), meanwhile the ‘sun’ and ‘shade’ leaf surfaces have different permeabilities to organic pollutants, with the ‘sun’ leaf surfaces being less permeable than the ‘shade’ ones [35]. And in the environment, most of the organic pollutants adsorbed on the upper surfaces were exposed to sunlight instead of the lower ones. In our experiment, therefore, the photolysis progress of Fla adsorbed on the upper leaf surfaces of the three mangrove species were mainly investigated. Experimental results were shown in Figs. 3, 4 and 5, Tables 2 and 3. Where C_0 is the initial concentration of Fla introduced onto the

Table 2 The kinetic parameters for the disappearance of Fla adsorbed on mangrove leaves ($n=9$)

Mangrove	Fla (ng/spot)	K_T (min^{-1})	R_t^2	K_C (min^{-1})	R_c^2	K_p (min^{-1})	$t_{1/2}$ (photolysis) (min)
<i>Kc</i>	20	0.0112	0.9705	0.0002	0.8899	0.0110	63.01
	200	0.0104	0.9830	0.0004	0.9223	0.0100	69.31
	400	0.0108	0.9836	0.0004	0.9414	0.0104	66.65
<i>Ea</i>	20	0.0255	0.9618	0.0006	0.9548	0.0249	27.84
	200	0.0349	0.9506	0.0008	0.9305	0.0341	20.33
	400	0.0345	0.9679	0.0005	0.9689	0.0340	20.39
<i>Ac</i>	20	0.0529	0.9461	0.0045	0.9068	0.0484	14.32
	200	0.0483	0.9648	0.0051	0.8902	0.0432	16.04
	400	0.0406	0.9950	0.0037	0.9708	0.0369	18.78

Table 3 Changes in the amount of Fla adsorbed on mangrove leaves under darkness and light conditions ($n=9$)

Mangrove	C_0 Fla(ng/spot)	C_T Fla(ng/spot)	C_{CF} Fla(ng/spot)	ΔC_T Fla(ng/spot)	ΔC_C Fla(ng/spot)	ΔC_P Fla(ng/spot)
<i>Kc</i>	20	5.88	19.52	14.12	0.48	13.64
	200	21.76	183.32	178.24	16.68	161.56
	400	31.13	360.14	368.87	39.86	329.01
<i>Ea</i>	20	3.45	19.00	16.55	1.00	15.00
	200	11.63	187.15	188.37	12.85	175.52
	400	16.80	382.85	383.20	17.15	366.05
<i>Ac</i>	20	2.73	16.93	17.27	3.07	14.20
	200	24.09	156.38	175.91	43.62	132.29
	400	35.96	326.44	364.04	73.56	290.48

C_T : the total final concentration of Fla at the end of the experiment

C_{CF} : the final concentration of Fla at the end of the control experiment

ΔC_T : the total disappearance amount of Fla at the end of the experiment, $\Delta C_T=C_0-C_T$

ΔC_C : the disappearance amount of Fla at the end of the control experiment, $\Delta C_C=C_0-C_{CF}$

ΔC_P : the amount of Fla photolysis at the end of the experiment, $\Delta C_P=\Delta C_T-\Delta C_C$

mangrove leaves. C_t is the concentration of Fla at time ‘t’ during the photolysis period.

From Figs. 3, 4 and 5, it can be seen that the curves for $\ln(C_0/C_t)$ of the Fla adsorbed on mangrove leaves versus time essentially yielded straight lines. Therefore, it was reasonable that the photolysis of different initial concentration of Fla adsorbed on mangrove leaves followed first-order kinetics. R_T^2 values listed in Table 2 were taken as a measure of the goodness of fit for the total illumination period, and R_C^2 values were taken as a measure of the goodness of fit for the control experiments.

From Table 2, the photolysis rate constant (K_P) can be calculated by subtracting K_T from K_C . K_T stands for the total disappearance rate constant of Fla adsorbed on the leaf surfaces, and K_C stands for the disappearance rate constant for Fla in the control experiments. It can be seen that the values of K_P were much bigger than that of K_C , which indicated that photolysis of Fla adsorbed on mangrove

leaves was the main environmental fate pathway compared to volatilization and absorption for its disappearance.

From Table 2, as for the same mangrove species, the half lives for the different initial concentrations of Fla adsorbed on the leaf surfaces were different. SPSS software was used to make sure whether there was a significant difference between them or not. The results showed that $p>0.05$ which meant that the initial concentrations of Fla adsorbed on the leaves of the same mangrove species did not affect the K_P values. The photolysis rates of Fla adsorbed on different mangrove species were in the order of $Ac > Ea > Kc$, with half-lives calculated by the formula of $t_{1/2}=\ln 2/K_P$ among 14.32–18.78, 20.33–27.84, and 63.00–69.31 min, respectively.

From Table 3, it can be seen that decreases of the Fla adsorbed on the leaves caused by photolysis were much bigger than those by volatilization or penetration into the inner parts of mangrove leaves. In other words, the disappearance of the Fla adsorbed on the leaves by volatilization and leaf absorption was negligible. Thus, it can be further concluded that the disappearance of the Fla adsorbed on mangrove leaves was mainly caused by

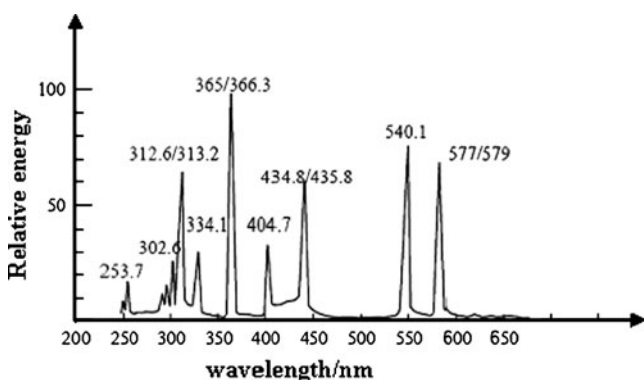


Fig. 6 Energy distributed curve of high pressure mercury lamp used in the experiment

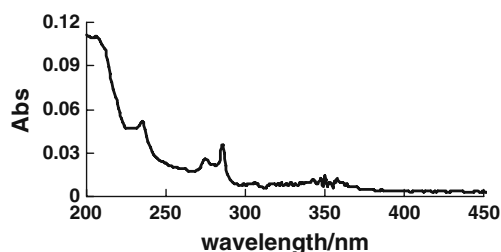


Fig. 7 UV-vis spectrum of Fla dissolved in Milli-Q water ($C=0.2$ mg/L)

Table 4 Photodegradation rates determined in this study, normalized to average conditions and related to other studies

PAH	Mangrove	Photolysis half-lives of Fla (h)					
		Measured in average value	Normalized data ^a	Literature data for spruce, pine needles and <i>Zea mays</i>			
				Niu et al. [24]	Niu et al. [25]	Wang et al. [26]	Edward et al. [37] (normalized data)
	<i>Kc</i>	1.11	48.8				
Fla	<i>Ea</i>	0.38	16.7	26	151	25.6	9.6
	<i>Ac</i>	0.27	11.9				

^aNormalized for temperature and light, to derive photodegradation half-lives on mangrove leaves under the average conditions in previous researches

photolysis, which was the main pathway for the transformation of the Fla adsorbed on mangrove leaves.

Also from Table 3, it can be seen that the photolysis of the Fla adsorbed on different mangrove species leaves was not completed at the end of the experiments. The reason might be that photolysis of the Fla adsorbed on leaf surfaces takes place predominantly in the cuticle and especially the cuticular wax of the leaves [22, 36]. Near the end of the experiments, a small amount of Fla might penetrate into the inner parts of the leaves [37] and it would be difficult for this amount of Fla to be photolyzed.

Photolysis Half-Lives of the Fla Adsorbed on Different Mangrove Leaves

Comparing with the previous studies [24–26], the half-lives of the Fla in our experiments were much smaller. The possible reasons might be as follows: most of the light emitted by the mercury lamp was in UV-band with its highest energy at 365 nm (Fig. 6). From Fig. 7, it can be seen that the main absorbance of Fla was located in the wavelength from 200 to 380 nm that belong to the UV-band of the sunlight reaching the earth’s surface. This illustrated that Fla adsorbed on mangrove leaves can be directly photolyzed under the irradiation of mercury lamp. The light intensity used in this study was much higher than that of in previous studies [24–26], which led to a higher photolysis rate of Fla adsorbed on mangrove leaves. In a sunny day, the light intensity of sunlight reaching the earth’s surface was about 10×10^4 lx with only about 4% of the total energy from the sunlight in the UV band [25]. According to the methods showed in reference 34 and 38, after normalizing the experimental condition to the previous studies, the photolysis rates of Fla in this paper are about 44 times of those measured in the previous studies (see Table 4).

Table 4 showed that there were still some differences between our normalized data and those of in the previous studies. The photochemical behavior of PAHs is strongly dependent on the feature of the surface upon which the compound is sorbed [38]. Different vegetations were used

in the published references, the microstructure, the composition and solar-selective absorption of the leaf-wax of the different leaves would also influence the results [24–26, 36].

The UV-vis Absorption Characteristics of the Leaf-Wax

As mentioned above, different photolysis rates of the Fla adsorbed on different mangrove leaves were observed. In order to understand more of these phenomena, UV-vis spectra of leaf-wax obtained from the three mangrove species dissolved in chloroform, while chloroform as a reference, were scanned by the established method. Results were shown in Fig. 8. From Fig. 8, it can be seen that three kinds of leaf-wax had their own special absorption located in the wavelength from 250 to 350 nm. As for the same amount of leaf-wax, the light absorption capacities of the three types of leaf-wax were in the order of $Kc > Ea > Ac$, which was in the reverse order to the photolysis rates of Fla adsorbed on the leaves of the three mangrove species. Some researchers showed that the leaf cuticle and wax can filter, scatter and focus certain wavelengths of the light source [39, 40]. As Fla was introduced onto the leaf surfaces and directly illuminated under the mercury lamp light, some of the mercury light reaching on mangrove leaves would be scattered or absorbed by mangrove leaves, and then, the illumination intensity on the Fla absorbed on the leaf surfaces would be decreased and the photolysis rate of Fla

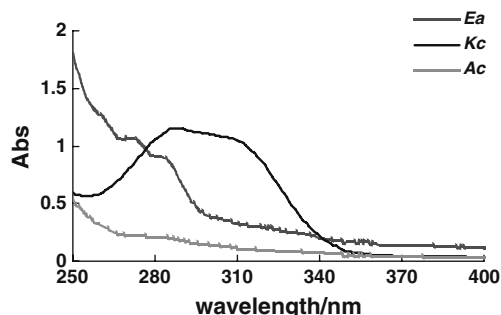


Fig. 8 UV-vis spectra of the leaf wax of three mangrove species dissolved in $CHCl_3$ ($C=3.9 \times 10^{-4}$ g/mL)

could be slowed down. This might be indicated that the light emitted by the mercury lamp and being absorbed or scattered by the leaf-wax could be another important reason for the differences in the photolysis rates of Fla adsorbed on different mangrove leaves.

Conclusion

Using the established fiber-optic fluorimetry, the Fla adsorbed on the leaf surfaces of the three mangrove species were directly determined. Meanwhile, the photolysis processes of Fla adsorbed on the leaf surface of three mangrove species were also investigated for the first time. The experimental results showed that the established method is simple, accurate and easy operating for the determination of Fla adsorbed on mangrove leaves. Results also showed the photolysis of the Fla adsorbed on mangrove leaves followed first-order kinetics with their photolysis rates on leaf surfaces in the order of $A_c > E_a > K_c$. The initial concentration of Fla absorbed on the leaf surface didn't influence the photolysis rate on the same mangrove species. Different structure of leaf-wax and their contains have different capacities to absorb or scatter the light form mercury lamp, and that may be an important reason for the differences between the photolysis rates of Fla adsorbed on different mangrove leaves. The results also indicated that photolysis of the Fla adsorbed on mangrove leaves was the main disappearance pathway of Fla adsorbed, only a small amount of Fla adsorbed on the leave surface disappeared by volatilization or absorption by the mangrove leaves.

Compared to the methods showed in references 20 and 24–26, great advantages were obtained for the established method. Firstly, comparing with the traditional methods, such as GC/MS, GC and HPLC which need an extraction of samples before analysis, the original existing forms and the distribution of Fla adsorbed on the leaf surfaces can be easily in situ determined. Secondly, for each sample, it only needs less than 1 min to analysis and without complex sample pretreatment, which indicated that the method was environmental friendly, time-saving and easy to operate. Thirdly, once the experimental conditions were further optimized and the sensitive of the method were improved, the established method has a great potential to be used in field.

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