Photodegradation of pyrene on soil surfaces under UV light irradiation

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ARTICLE INFO

ABSTRACT

The rates of photodegradation of pyrene (Pyr) on soil surfaces under UV light have been studied. Different parameters such as temperature, soil particle sizes, soil depth, and humic acid (HA) concentration responsible for photodegradation have been monitored. The results obtained indicated that Pyr photodegradation follows pseudo-first-order kinetics. Pyr degradation was fastest at 30 °C, while the photodegradation rate was increased with the temperature from 20 to 30 °C. The degradation loss was about 35% at 30 °C, 30% at 25 °C and 25% at 20 °C, respectively. The rates of Pyr photodegradation at different soil particle sizes followed the order: less than 1 mm > less than 0.45 mm > less than 0.25 mm. The results showed that the relationship of Pyr half-life with soil depth was linear (significant correlation, $p < 0.01$). When the soil depth increased from 1 to 4 mm, the half-life increased from 19.80 to 37.46 d. HA treatments significantly increased the photodegradation of Pyr on soil surfaces under UV light. However the concentration of HA increased from 5 to 40 mg kg^{-1}, the pseudo-first-order rates of Pyr decreased due to the shielding effect of HA.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of major contaminants that are ubiquitous in the environment. In industrial countries, anthropogenic activities are a principal source of PAHs in soil [1,2]. PAHs, especially those with four or more rings and their metabolites, are considered as hazardous pollutants due to their toxicity, mutagenicity and carcinogenicity, and are classified as compounds with significant human health risk [3]. Pyrene (Pyr) is a typical high molecular weight (HMW) PAH with four rings, and it has been classified by the US Environmental Protection Agency (USEPA) as a priority pollutant [4]. While not as active a carcinogen as benzo[a]pyrene, pyrene is an important mutagen prevalent in contaminated soil [5].

The main processes which successfully remove and eliminate PAHs from the environment include: microbiological transformation and degradation, volatilization, photo-oxidation, chemical oxidation, bioaccumulation and biological uptake [6,7]. However some of the HMW PAHs are recalcitrant, as biological processes are always ineffective in removing them. Photodegradation is an important transformation pathway for most PAHs in the environment. The photolysis rate of selected PAHs is relatively fast [8], because this process preferentially attacks the same tertiary carbon atoms that tend to block biodegradation [9].

Several methods based on chemical [10,11] and biological [12–14] destruction of Pyr have been proposed and tested. However, chemical methods may cause contamination again, while biological methods need long time. Methods based on photolytic degradation could be effective and easy as well. Pyr photodegradation has essentially been studied in different liquid media [15–17], in diesel particulate matter and on the various adsorbent surfaces (alumina, silica gel, controlled pore size glass, flaked graphite and coal stack ashes) from the vapor phase [18,19], but little is known about the photochemical behavior of Pyr on soil surfaces.

The photodegradation of organic compounds on soil are affected by many factors. Balmer et al. [20] found that soil particle size, mineral composition, light absorption characteristics, and moisture content affected the nature of soil photoreactions of pesticides. Because light penetration into soils is very limited [21,22] and is wavelength dependent, the fraction of total compound actually exposed to light depends on the type of soil, on the thickness of the soil layer, and on the light absorption spectrum of the compound. Since temperature and humidity strongly influence the compound's sorption behavior and rate of disappearance from soil [23], these parameters also need to be considered. Photolysis rates and phototransformation products are actually dependent on the intensity and wavelength distribution of the light used [24]. Humic acids (HAs) are complex organic molecules produced by the decomposition of plant and animals remained in soil, they can either enhance [25] or inhibit photolysis [26].

In this paper, main factors that influence the photodegradation of Pyr on soil surfaces such as temperature, soil particle size, soil

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thickness and humic acid were investigated under irradiation of UV light.

2. Materials and methods

2.1. Chemicals

Pyrene (Pyr, 97%) was purchased from Fluka, Germany, and used without further purification. The physical–chemical properties of Pyr were as follows: No. of rings 4, melting point 149 °C, boiling point 360 °C, aqueous solubility 0.14 mg l^{-1}, logarithm of the octanol:water partitioning coefficient 5.32, Vapour pressure (torr at 20 °C) 6.80×10^{-7}. Methanol (HPLC grade) was purchased from Shandong Yuwang Company, China. Hexane ($CH_3(CH_2)_4CH_3$) and dichloromethane (CH_2Cl_2) were purchased from Tianjin Concord Technical Company, China. Humic acid was purchased from Tianjin Jinke Company, China.

2.2. Experimental soil

Surface soil sample (top 10 cm) was collected from the Ecological Station of the Shenyang Institute of Applied Ecology, Chinese Academy of Sciences. After being air-dried, soil samples were divided into different particle sizes by passing them through 1, 0.45 and 0.25 mm sieves, respectively. To prepare a sterile soil, the sieved soil was autoclaved at 121 °C for 30 min twice, and stored in the dark before use. The soil had the following physical characteristics: pH 6.80, total organic carbon 1.78%, sand 21.40%, silt 46.50% and clay 32.10%, bulk density 2.53 g cm^{-3}.

The soil sample was spiked with a methanol solution of Pyr, mixed thoroughly and then air-dried for the evaporation of methanol. The concentration of Pyr was designed to be 40 mg kg^{-1} in the soil.

2.3. Photodegradation chamber

Photodegradation studies were performed in a chamber as shown in Fig. 1. In parallel, two arrays of nine UV lamps were fixed in the top and middle of the chamber, respectively, with a distance of 60 mm between two lamps in the same array. The distance between the lamps and samples was 150 mm. Wavelength of UV lamps used throughout all the experiments was 254 nm. Petri dishes containing experimental soil samples were placed on the shelves for photo-irradiation. The temperature within the chamber was adjusted through refrigerator, heater, and fans in the chamber. During different intervals of the exposure, three replicate samples and dark control samples were taken from the chamber and transferred into 100 ml Teflon tubes.

2.4. Photo-irradiation

2.4.1. Effect of chamber temperature

To study the influence of chamber temperature, five grams of soil samples of 1 mm particle size were evenly spread on the Petri dishes (9 cm in diameter) and replicated thrice. Chamber temperature varied from 20 to 30 °C. Light proof Petri dishes containing same soil samples were set as control for the measurement of non-photodegradated Pyr loss throughout all the experiments. The UV irradiation intensity was 1071 μW cm^{-1}. All the Petri dishes were randomly placed on the shelves, and sampling was performed during the irradiation with the sampled soil sacrificed.

2.4.2. Effect of soil particle size

To study the influence of soil particle sizes on the photodegradation of Pyr, five grams of soil samples of particle sizes 0.25, 0.45, and 1 mm respectively, were evenly spread on the Petri dishes (9 cm
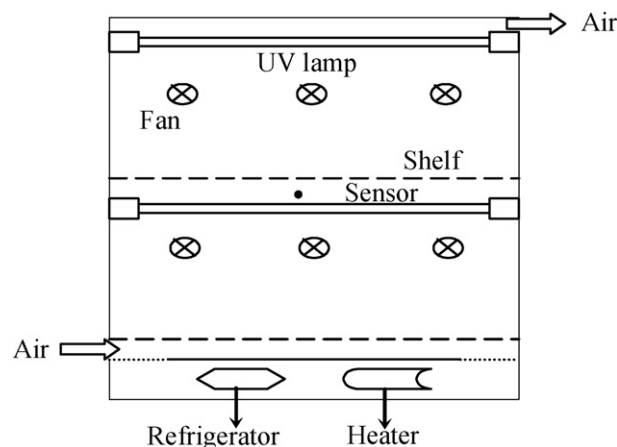

Fig. 1. Device for photodegradation of Pyr on soil surfaces.

in diameter) and replicated thrice. Chamber temperature was 30 °C throughout all the experiments. Irradiation, sampling, and analyses were then performed as described in Section 2.4.1.

2.4.3. Effect of soil depth

To test the effect of soil depth on photodegradation of Pyr, soil samples (size = 1 mm) at a weight of 2.5, 4, 5, 6, and 10 g were evenly spread on the Petri dishes (9 cm diameter), respectively. Three replicates were prepared. Soil depth was calculated using soil weight, soil bulk density, and bottom area of the Petri dishes. Irradiation, sampling, and analyses were then performed as described in Section 2.4.1.

2.4.4. Effect of humic acid

About 100 g of HA was dissolved in 0.1 M NaOH solution, diluted with 1000 ml distilled water as storage solution. Different dosages of HA storage solution were added to Pyr contaminated soil samples. The additive concentrations of HA in the soil samples were 5, 10, 20 and 40 mg kg^{-1}, respectively. About 5 g of soil samples of 1 mm particle size were evenly spread on the Petri dishes (9 cm in diameter) and replicated thrice. Irradiation, sampling, and analyses were then performed as described in Section 2.4.1.

2.5. Soil extraction and HPLC analysis

Concentrations of the Pyr in irradiated and non-irradiated samples were obtained by the following method. Soil samples were transferred into 100 ml Teflon tubes, and mixed with dichloromethane (1 g of soil: 5 ml of dichloromethane). Each sam-
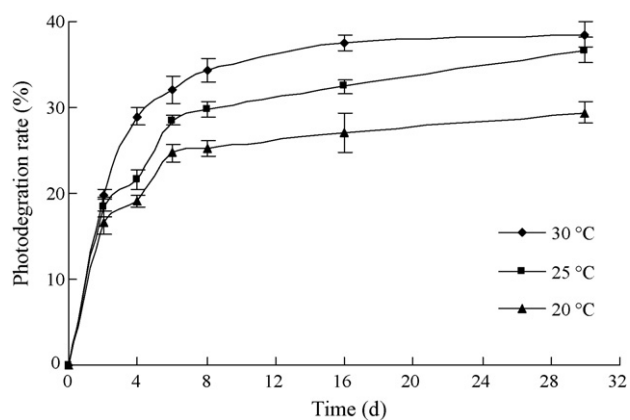
Fig. 2. The effect of temperature on Pyr photodegradation on soil surfaces under UV irradiation.

ple was extracted for 2 h in an ultrasonic bath, in which the water temperature was just lower than 40 °C. The mixture was then centrifuged at 4000 rpm for 5 min to separate the supernatant from the soil. An aliquot of 0.5 ml of extract was passed through a glass column containing 1 g of silica gel wetted with hexane. The extract was eluted with 1 and 2 ml mixture of hexane:dichloromethane (50:50, v/v) in turn. The eluate was completely dried under the gentle stream of nitrogen. The solid residue was re-dissolved in 1 ml of methanol for HPLC analysis. Quantification of Pyr in methanol solutions was done by an HPLC (Hewlett-Packard 1090-IISeries) with a diode array detector. The mobile phase used was methanol:water (85:15, v/v) at a flow rate of 0.8 ml min^{-1}, and detector wavelength was 241 nm. The injection volume was 10 μl. The extraction recovery of Pyr under the given conditions was higher than 92% (recovery experiments).

3. Results and discussion

3.1. The effect of chamber temperature

The photodegradation loss can be obtained from the following calculation:

$$L = \frac{C_N - C_I}{C_0} \times 100\% \qquad (1)$$

where L = photdegradation loss at time t, C_0 = original concentration of Pyr, C_N = concentration of Pyr non-irradiated soil sample at time t, C_I = concentration of Pyr irradiated sample at time t.

The photodegradation losses of Pyr versus time on soil surfaces at the temperature 30, 25 and 20 °C are shown in Fig. 2. Pyr degradation was fastest at 30 °C, while the photodegradation rate was increased with the temperature. The photodegradation loss of Pyr at the three temperatures increased rapidly during the first 8 d of the experiment, with the degradation loss being about 35% at 30 °C, 30% at 25 °C, and 25% at 20 °C, respectively. Our study showed that temperature greatly influenced the Pyr breakdown on the soil surface during UV irradiance. The reasons for this result may be that increased temperatures decreased PAHs sorption by soils [27] and increased their solubility and vapour pressure [28]. Moreover, temperature may influence the velocity of photochemical reaction. Maliszewska-Kordybach [29] investigated the effect of temperature on the range and rate of disappearance of four PAHs (fluorine, anthracene, pyrene and chrysene) added as a mixture of pure compounds to two different soils (light loam and loamy sand) and found that an increase in temperature from 10 to 25 °C enhanced the losses of all four PAHs from both soils. Our study showed similar results as the above indicating that increased temperature may
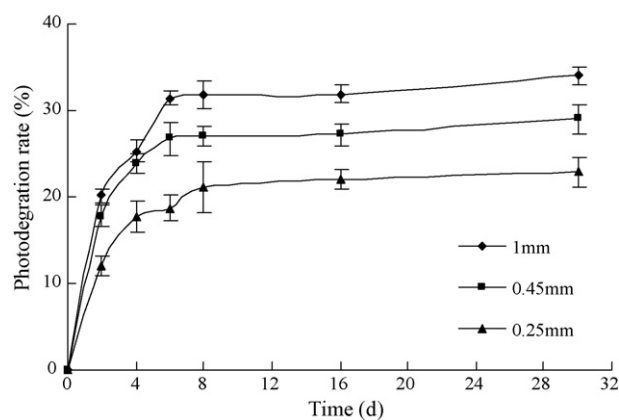
enhance the degradation loss of PAHs in soil. Coover and Sims [30] studied the influence of temperature on the apparent loss kinetics of 16 PAHs in an unacclimated agricultural soil and found that increasing the soil temperature in the range of 10–30 °C improved the rate and extent of apparent loss of lower molecular weight PAHs. Our study however showed a different result. The reason for this may be that the soil used in their study was contaminated with a mixture of 16 PAHs, while that of our study was contaminated by only one single PAH, hence antagonistic effects of PAHs did not exist.

3.2. Effect of soil particle size

Soil particle sizes influence the sorption and desorption of PAHs in soil. Therefore, we also used photodegradation losses to show the results. The photodegradation loss can be obtained from the Eq. (1). In this study, we chose three different soil particle sizes (diameter less than 1 mm, less than 0.45 mm, and less than 0.25 mm). Fig. 3 is a graphical comparison of the Pyr photodegradation losses at different soil particle sizes. Fig. 3 clearly showed that soil particle size influenced the photodegradation. Pyr degradation was fastest when soil particle size was less than 1 mm. The rates of Pyr photodegradation at different soil particle size followed the order: less than 1 mm > less than 0.45 mm > less than 0.25 mm. These results were similar to those obtained for the photolytic losses of cypermethrin, deltamethrin, and fenvalerate at different soil particle sizes, where the photodegradation loss for diameter less than 1 mm soil sample was fastest and that for less than 0.25 mm soil sample was slowest [31]. Soil particles less than 1 mm are more loosely packed, leaving more room for light to scatter and permeate the soil than the other two soil particle sizes. Our study was performed on air-dried soil, so the photodegradation by hydroxyl radical was almost eliminated [32]. Singlet oxygen plays a main role in photodegradation. The singlet oxygen penetration is dependent upon soil porosity and soil depth. However, a different behavior was observed for PAHs photodegradation in the clay soil, where PAHs photodegradation was not affected by particle size in the clay soil [33]. The particle ranges they studied were 0.05–0.08 and 0.08–0.12 mm, which, in fact, were too small to express the difference between the particles. In the current experiment, the photodegradation losses of all treatments did not show any significant change after 8–10 d irradiation, indicating that direct photodegradation was no longer happening, while indirect photodegradation proceeded slowly.

3.3. Effect of soil depth

Soil depth is an important to be considered in a photolysis study. The photodegradation rate is determined not only by photolysis,

Fig. 3. The Pyr photodegradation of different soil particle sizes under UV irradiation.

Table 1
Kinetic parameters for Pyr photodegradation at different soil depth.

Soil depth (mm)	k (1×10^{-2} d^{-1})	$t_{1/2}$ (d)	r
1.0	3.50	19.80	0.9548
1.6	3.01	23.03	0.9560
2.0	2.52	27.50	0.9380
2.4	2.15	32.24	0.9579
4.0	1.85	37.46	0.9458

Table 2
The effect of different HA concentrations on the dynamical parameters of Pyr photodegradation.

HA concentration (mg kg^{-1})	Kinetic model	k (h^{-1})	$t_{1/2}$ (h)	r^2
0	$C_t = 98.53e^{-0.0011t}$	0.0011	630.09	0.9626
5	$C_t = 94.19e^{-0.0062t}$	0.0062	111.79	0.9658
10	$C_t = 95.34e^{-0.0054t}$	0.0054	128.35	0.9707
20	$C_t = 97.04e^{-0.0049t}$	0.0049	141.45	0.9716
40	$C_t = 96.35e^{-0.0041t}$	0.0041	169.05	0.9738

but also it is a function of the layer thickness of soil [20]. Photodegradation of organic contaminants in soil will be restricted to a certain thickness, which depends on many factors such as light wavelength distribution, soil characteristics, and photodegradation mechanism [20,21]. In this experiment, five thickness levels (1.0, 1.6, 2.0, 2.4, and 4.0 mm) were tested.

Many factors influence the photodegradation of Pyr on soil surfaces such as temperature, soil particle size, soil thickness and humic acid, but in general Pyr photodegradation were fitted to the first-order equation [34]:

$$\ln \frac{C_0}{C} = kt \tag{2}$$

where C_0 and C are the Pyr concentration at times zero and t respectively, and k is the rate constant. First-order degradation rate constants were determined by analysis. Half-lives $t_{1/2}$ were calculated using Eq. (3) which was derived from Eq. (2) by replacing C with $C_0/2$:

$$t_{1/2} = \ln \frac{2}{k} = \frac{0.6931}{k} \tag{3}$$

The results of kinetic parameters for Pyr photodegradation are listed in Table 1. It shows that increasing depth of soil sample leads to an increase in half-life ($t_{1/2}$) and a decrease in rate constant (k). When the soil depth increased from 1 to 4 mm, the half-life increased from 19.80 to 37.46 d. Researchers that have studied the photodegradation of other organic contaminants have obtained the similar results [20,22,35,36]. Our results showed that the relationship of Pyr half-life with soil depth was linear (significant correlation, $p < 0.01$). Soil depth had a much great effect on photodegradation in soil because it influenced the light penetration and soil ventilation. Frank et al. [36] studied the effects of soil depth and moisture on niclosamide photolysis. They concluded that when moisture was maintained, only a gradual increase in half-life with soil depth was observed, and the relationship of that increase with depth was strongly linear.

The study about toxicity of the oxidation intermediates may be important in the photodegradation processes of Pyr. Bioassay using *Vibrio fischeri* has been shown to be a rapid, sensitive and cost effective method by many researches [37–39]. In further study, we would carry out some works about toxicity evaluation of the oxidation intermediates.

3.4. Effect of HA concentration

Humic acids (HAs) are complex organic molecules produced by the decomposition of plant and animals remained in soil, they can either enhance [25,40–42] or inhibit photolysis [26,35,43]. The influence of HA on the photodegradation of Pyr on soil surfaces was investigated herein. Effect of HA was examined by the experiments that were undertaken using the same initial concentration of Pyr and various concentrations of additive HA. The pseudo-first-order constants of photodegradation of Pyr corresponding to different dosages of the HA are presented in Table 2. Clearly, all HA treatments significantly increased the photodegradation of Pyr on soil surfaces under UV light. However in our experiment lower HA treatment is better that higher HA treatment. When humic

substances absorbed UV irradiation, the reactive oxygen intermediates were generated and, therefore, may attack chemicals in the environments and initiate their degradation [24,44]. As the concentration of HA increased from 5 to 40 mg kg^{-1}, the pseudo-first-order rates (shown as k) of Pyr decreased (Table 2) due to the shielding effect of HA, which protested Pyr from incident radiation, thus retarded the photodegradation. With the compound concentration increasing, the attenuation (absorption) of incident light by non-target substances should be a critical factor that influenced the photodegradation rate.

4. Conclusion

Photodegradation is a major degradation process which can naturally clean up the soil. Photodegradation rate of Pyr is affected by soil characteristics and environmental factors. According to our study, Pyr photodegradation follows pseudo-first-order kinetics, and soil depth has a much great effect on photodegradation of Pyr in soil. The rate constant of photodegradation ranged from 3.50 to 1.85×10^{-2} d^{-1} within a soil depth of 1.0–4.0 mm. In addition, the increase of soil particle sizes left more room for light to scatter and permeate the soil thereby speeding up the photodegradation. The Pyr loss of photodegradation at 30 °C was greater than those at 25 and 20 °C. HA treatments significantly increased the photodegradation of Pyr on soil surfaces under UV light. However the concentration of HA increased from 5 to 40 mg kg^{-1}, the pseudo-first-order rates of Pyr decreased due to the shielding effect of HA, which protested Pyr from incident radiation.

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