



## Photolysis of Phenanthrene on Soil Surfaces Under UV-Irradiation

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Received: 21 November 2013;

Accepted: 13 March 2014;

Published online: 26 December 2014;

AJC-16515

The photolysis of phenanthrene on soil surfaces under UV-irradiation was investigated. The effects of organic matter, oxygen, soil moisture and soil salinity on the degradation of phenanthrene were observed. The results showed that the organic matter, oxygen and soil moisture enhanced the degradation of phenanthrene through different ways, while the salinity depressed the degradation. The photolysis of phenanthrene on soil surfaces in the presence of oxygen followed pseudo-first-order kinetics. The possible mechanisms of photolysis of phenanthrene on soil surfaces might include direct photolysis, photosensitized reactions and photo-oxidation.

**Keywords:** Photolysis, Phenanthrene, Soil, UV-irradiation.

### INTRODUCTION

Phenanthrene is a compound of polycyclic aromatic hydrocarbons consisting of two or more fused benzene rings. Polycyclic aromatic hydrocarbons are hazardous materials because of their mutagenic and carcinogenic properties and are widely distributed in the environment through combustion, discharge of fossil fuels, automobile emissions and subsequent atmospheric transport and deposition<sup>1-5</sup>. Because they are hazardous to ecosystems and human health, it is important to investigate the fate of polycyclic aromatic hydrocarbons in the environment and find ways to eliminate them<sup>6-8</sup>.

Several processes which successfully remove and eliminate polycyclic aromatic hydrocarbons from the environment include microbiological transformation and degradation, volatilization and photolysis<sup>9,10</sup>. Photolysis is one of the major abiotic transformation processes for polycyclic aromatic hydrocarbons in the environment<sup>11</sup>. In the past few years, there had been many studies investigating the photodegradation of polycyclic aromatic hydrocarbons in aqueous solutions<sup>12-18</sup> and in atmospheric aerosols<sup>19</sup>. A number of studies on the adsorption of polycyclic aromatic hydrocarbons on silica, alumina and Fe<sub>2</sub>O<sub>3</sub> had also been reported<sup>20,21</sup>. The mechanisms of photolysis of polycyclic aromatic hydrocarbons were described by Miller and Olejnik<sup>22</sup> and An and Carraway<sup>23</sup> in an aqueous phase. Jang and Mcdow<sup>24</sup> reported the products of photolysis of polycyclic aromatic hydrocarbons in atmospheric aerosols

and therefore concluded the mechanisms of photolysis of polycyclic aromatic hydrocarbons in atmospheric aerosols. Debestani *et al.*<sup>25</sup> reported that the products and mechanisms of photolysis of anthracene on dry surfaces in the absence and presence of oxygen. However, comparatively less research has been directed at examining photodegradation of polycyclic aromatic hydrocarbons on soil surfaces and less is known about the mechanisms of photolysis of polycyclic aromatic hydrocarbons on soil.

In this paper, the result of the photolysis of phenanthrene on soil surfaces in the absence and presence of oxygen under UV-irradiation was investigated. The main influencing factors, such as organic matter, oxygen, soil moisture and soil salinity, were taken into consideration. Furthermore, the possible mechanisms of photolysis of phenanthrene on soil surfaces was discussed.

### EXPERIMENTAL

Phenanthrene (97 %) was purchased from Fluka, Germany and used without further purification. Methanol (Chromatography grade) was purchased from Shandong Yuwang Company, China. Hexane and dichloromethane (Analytical grade) were purchased from Tianjin Concord Technical Company, China.

Surface soil samples (0-10 cm) were collected from the Ecological Station of the Shenyang, Institute of Applied Ecology, Chinese Academy of Sciences. The soil samples were

sterilized by soaking in  $\text{NaN}_3$  solution for about 48 h and then dried in an oven at  $105^\circ\text{C}$ . After drying, the soil samples were passed through a 1 mm sieve. The sieved soil samples were then stored in a dark chamber before use. The physical properties of the experimental soil samples are presented in Table-1. Mineral components of the experimental soil samples were analyzed by X-ray fluorescence (XRF) and the results were listed in Table-2.

TABLE-1  
PHYSICAL PROPERTIES OF THE EXPERIMENTAL SOIL

pH	TOC (%)	Texture (%)			Bulk density ( $\text{g cm}^{-3}$ )
		Sand	Silt	Clay	
6.8	1.78	21.4	46.5	32.1	2.53

TABLE-2  
MAIN ELEMENTS AND COMPONENTS  
OF THE EXPERIMENTAL SOIL

Element	Concentration ( $\text{mg kg}^{-1}$ )	Element	Concentration ( $\text{mg kg}^{-1}$ )	Component	Concentration (%)
As	8.95	Ni	26.70	$\text{SiO}_2$	68.22
Ba	676.65	P	630.30	$\text{Al}_2\text{O}_3$	13.41
Ce	123.00	Pb	37.00	$\text{Fe}_2\text{O}_3$	4.19
Cl	49.55	Rb	109.75	MgO	1.13
Co	11.70	Sr	189.75	CaO	1.16
Cr	67.65	Th	13.00	$\text{Na}_2\text{O}$	1.78
Cu	36.70	Ti	4,459.40	$\text{K}_2\text{O}$	2.43
Ga	17.90	Zn	70.45	–	–
La	65.90	Zr	276.95	–	–
Mn	577.70	V	76.35	–	–

Some of the sieved soil samples were further treated with heat at  $800^\circ\text{C}$  for 48 h to destroy any organic matter. The residual organic matter of the heat-treated soil samples was undetectable.

For the individual experiments, the soil samples were treated with a methanol solution of phenanthrene, mixed thoroughly and then air-dried to evaporate the methanol. The concentration of phenanthrene in the resulting soil samples was  $40 \text{ mg kg}^{-1}$ .

**Photolysis experiments:** The photolysis experiments were conducted using a YQX-1 anaerobic photodegradation chamber (Yuejing Company, China) with two UV lamps fixed at the top and separated by 60 mm. The UV lamps (Phillips ATLD 20W, Model UVA) had a wavelength of 253.7 nm. In all photolysis experiments, three replicates of 5 g of soil samples were evenly spread on Petri dishes and randomly located in the anaerobic photodegradation chamber under the UV lamps. Light proof Petri dishes also containing 5 g of uniformly spread soil samples were used as controls for the measurement of non-photolytic phenanthrene loss for all experimental treatments. Nitrogen gas was used to de-aerate oxygen from the chamber for the anaerobic photodegradation treatments. Petri dishes containing soil samples were placed on the shelves for UV-irradiation. The height of the lamps above the soil samples was 450 mm. Temperature within the chamber was held at  $25^\circ\text{C}$  using a heater and fans throughout all experiments. Soil samples were taken at 1 day intervals from the Petri dishes exposed to UV light.

The effects of oxygen, soil moisture and soil salinity on the degradation of phenanthrene under air condition were also examined. For the latter experiments, the soil samples on the Petri dishes were treated with a fine spray of water or solutions of potassium bromide to give the desired degree (by weight) of moisture and salinity.

**Phenanthrene extraction procedure:** Concentrations of phenanthrene in the irradiated and non-irradiated soil samples were obtained by the following method: The soil samples were transferred into 100 mL Teflon tubes and mixed with 20 mL dichloromethane. Each sample was extracted for 2 h in an ultrasonic bath in which the water temperature was lower than  $35^\circ\text{C}$ . The mixtures were then centrifuged at 4000 rpm for 5 min to separate the supernatant from the soil samples. An aliquot of 0.5 mL of extraction was passed through a glass column containing 0.9 g of silica gel wetted with hexane. The extraction was eluted with 1 mL hexane: dichloromethane (1:1, v/v) four times. The eluate was completely dried under a gentle stream of nitrogen. The solid residue was re-dissolved in 1 mL of methanol for HPLC analysis.

**Analytical methods:** Quantification of phenanthrene in methanol solutions were conducted using an Agilent model 1200 HPLC with a variable wavelength detector set at 250 nm (Agilent Technologies, Shenyang, China). The mobile phase used was methanol: water (90:10, v/v) at a flow rate of  $0.7 \text{ mL min}^{-1}$ . Injection volume was  $10 \mu\text{L}$ . Three replicates were performed for analysis.

Organic matter was determined using a Vario EL III (Elementar Analysensysteme GmbH, Hanau, Germany) TOC analyzer.

## RESULTS AND DISCUSSION

### Effect of organic matter under anaerobic conditions:

The degradation over a 6 day period of phenanthrene on the heat-treated and natural soil surfaces under anaerobic conditions was examined as shown in Fig. 1. The degradation percentages of phenanthrene on both the heat-treated and natural soil surfaces increased with increasing irradiation time, with the degradation on the natural soil always being slightly greater.

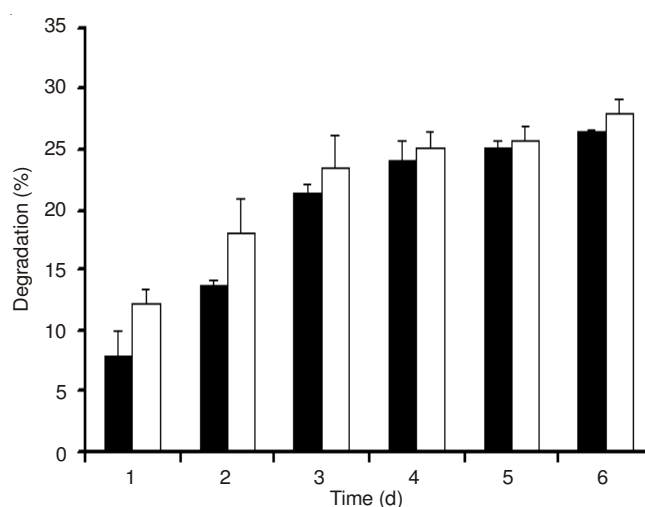


Fig.1. Photolysis of phenanthrene on the heat-treated and natural soil surfaces under anaerobic conditions; (■): The heat-treated soil surfaces (□): the natural soil surfaces

In the heat-treated soil, organic matter is absent. Since the degradation percentages of phenanthrene on the heat-treated soil surfaces are always lower than the degradation percentages of phenanthrene on the natural soil surfaces under anaerobic conditions, organic matter therefore enhances the photolysis of phenanthrene on soil surfaces under anaerobic conditions. Photolysis of phenanthrene on the heat-treated soil surfaces is therefore likely to be due to photon absorption by the phenanthrene molecules causing excitation leading to direct photolysis. Similar results have been reported by Debestani *et al.*<sup>25</sup>.

Soil organic matter includes humic substances (HS). Humic substances is known to act as photosensitizer in water to enhance the photolysis of phenanthrene via energy transfer, as has been reported by Wang *et al.*<sup>26</sup>. In the natural soil, photons can also be absorbed by the humic substances molecules causing their excitation and the excited humic substances molecules can lead to rapid photosensitized reactions of phenanthrene molecules *via* energy transfer from humic substances molecules in their triplet states. Thus the photolysis of phenanthrene on the natural soil surfaces under anaerobic conditions is the result of both direct photolysis and photosensitized reactions. However, the effect of the photosensitized reactions of phenanthrene is minor in comparison with the effect of the direct photolysis of phenanthrene.

**Effect of oxygen:** A comparison of the degradation of phenanthrene in the absence and presence of oxygen over 5 days is shown in Fig. 2. The degradation percentages of phenanthrene on both treatments increased along with increasing irradiation time.

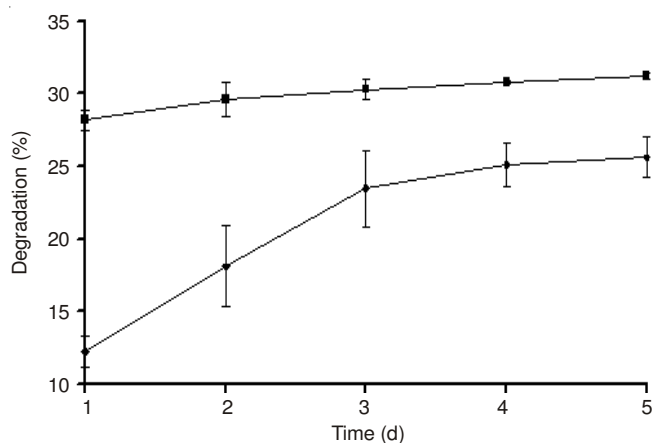


Fig. 2. Photolysis of phenanthrene under UV-irradiation in the presence of O<sub>2</sub> (■) and absence of O<sub>2</sub> (◆)

As well as direct photolysis and photosensitized reactions, phenanthrene can also undergo photooxidation, therefore the degradation percentages of phenanthrene in the presence of oxygen are consistently higher than the degradation percentages in the absence of oxygen.

According to Amama *et al.*<sup>27</sup>, the process of photooxidation includes the effects of superoxide radical anion (O<sub>2</sub><sup>•-</sup>) and singlet oxygen (<sup>1</sup>O<sub>2</sub>). When suitable compounds on the soil surfaces (including phenanthrene) are illuminated with UV light, electrons can be generated and these electrons can react with oxygen molecules to generate superoxide radical

anion (O<sub>2</sub><sup>•-</sup>). Singlet oxygen (<sup>1</sup>O<sub>2</sub>) is formed by transferred energy from excited humic substances or phenanthrene molecules. The formation of superoxide radical anion (O<sub>2</sub><sup>•-</sup>) and singlet oxygen (<sup>1</sup>O<sub>2</sub>) then directly leads to the oxidative degradation of phenanthrene on soil surfaces.

The pseudo-first-order rate equation is<sup>28</sup>,

$$-\ln \frac{C_t}{C_0} = kt \quad (1)$$

where C<sub>t</sub> and C<sub>0</sub> are the phenanthrene concentration at time t and zero, respectively and k is the rate constant.

The pseudo-first-order rate equation was applied to the experimental results as shown in Fig. 3. The correlation coefficient (r<sup>2</sup>) was 0.9545 which indicated that the photolysis of phenanthrene on soil surfaces in the presence of oxygen followed pseudo-first-order kinetics. The rate constant (k) was 0.0118 d<sup>-1</sup> and the half-life (t<sub>1/2</sub>) was 58.7 d.

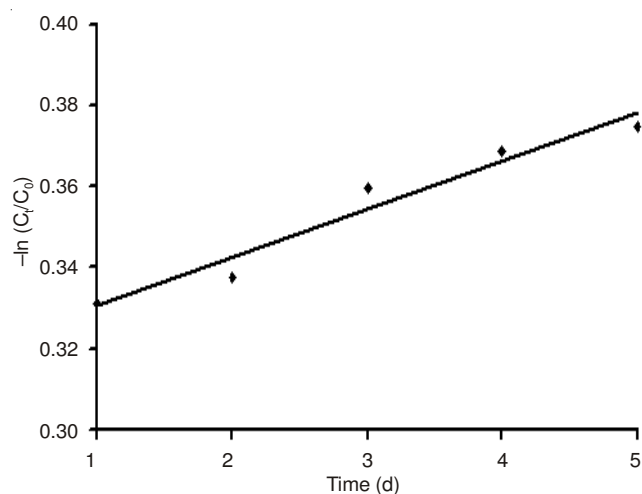


Fig. 3. Degradation kinetics of phenanthrene in presence of oxygen under UV-irradiation

**Effect of soil moisture:** The effect of soil moisture in the range of 0-20 % (w/w) on the degradation of phenanthrene was examined over 5 d. The results are shown in Fig. 4. The degradation percentages of phenanthrene increased along with increasing irradiation time for all three treatments. The level of soil moisture clearly enhanced the degradation of phenanthrene on soil surfaces.

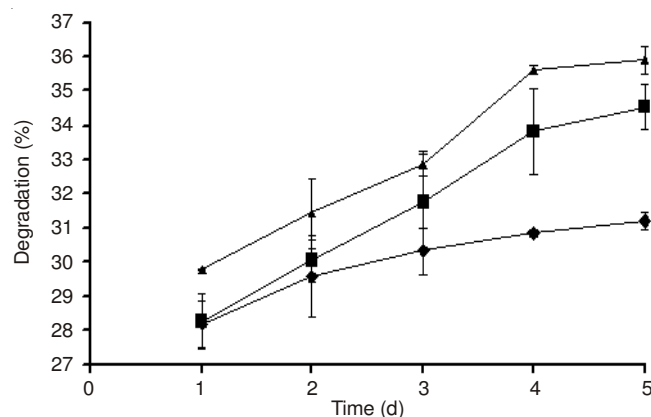


Fig. 4. Effect of soil moisture on phenanthrene degradation: (◆) 0 %, (■) 10 %, (▲) 20 %

Phenanthrene degrades even in conditions of low or no soil moisture because of direct photolysis, photosensitized reactions and photooxidation all contribute to the degradation. When the soil is moist, the degradation of phenanthrene increases with increasing soil moisture. Similar results have been reported by Hilarides *et al.*<sup>29</sup>, Shelton and Parkin<sup>30</sup>, Frank *et al.*<sup>31,32</sup>. There are three probable reasons contributing to this. Firstly, the superoxide radical anion ( $O_2^{\bullet-}$ ) can react with water ( $H_2O$ ) to produce hydroxyl radicals ( $OH^{\bullet}$ ) which can enhance the photolysis of phenanthrene on soil surfaces. Secondly, there is a direct radiation effect; water greatly increases the amount of radiation absorbed in the soil. Thirdly, with less water available, the mobility of the chemical is affected. There is less phenanthrene sorption and more diffusion in moist soils.

**Effect of salinity:** Effect of salinity in the range of 0-625  $\mu M$  on the degradation of phenanthrene was examined over a 5 day period. The results are shown in Fig. 5. The degradation percentages of phenanthrene increased along with increasing irradiation time for four treatments. The level of soil salinity clearly depressed the degradation of phenanthrene on soil surfaces.

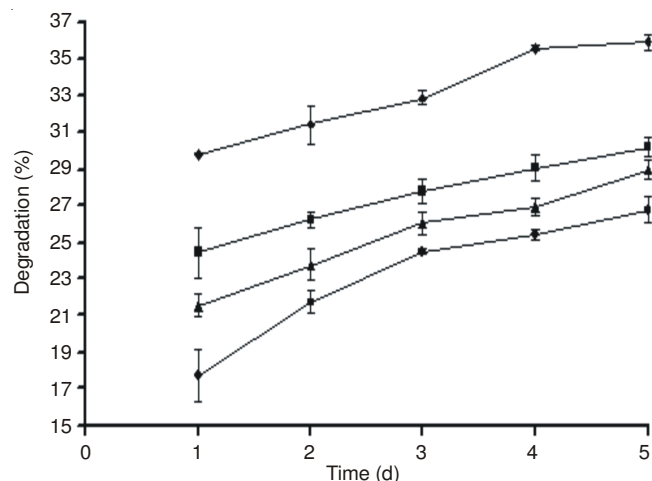


Fig. 5. Effect of salinity on phenanthrene degradation: (◆) 0 mM, (■) 62.5 mM, (▲) 250 mM, (●) 625 mM

A similar depression of degradation has been reported by Kong and Ferry<sup>33</sup>. The depression could be due to the quenching of singlet oxygen ( $^1O_2$ ) by bromide ion ( $Br^-$ ) which would reduce the concentration of singlet oxygen ( $^1O_2$ ) and thus the contribution of this component of the phenanthrene degradation.

**Possible degradation mechanisms:** Till now, there have not been well developed mechanisms or satisfactory explanation of the photolysis of phenanthrene on soil surfaces. It seems from this work that there are several pathways for the degradation-direct photolysis, photosensitized reactions and photooxidation by several species. The possible mechanisms of photolysis of phenanthrene on soil surfaces may be summarised as follows.

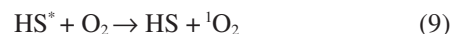
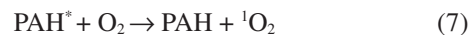
Firstly, photons absorbed by phenanthrene molecules cause their excitation. The excited phenanthrene molecules have the potential to undergo direct photolysis as shown in eqns. (2) and (3).



Secondly, the phenanthrene molecules have the potential to undergo photosensitized reactions as shown in eqns. (4) and (5). The phenanthrene molecules which absorb transferred energy from the humic substances molecules can then undergo photolysis according to eqn. (3):

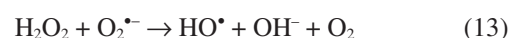
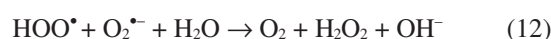
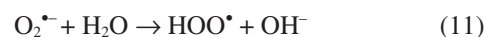


Thirdly, the phenanthrene molecules have the potential to undergo photooxidation with reactive oxygen species such as singlet oxygen ( $^1O_2$ ) or free radicals. There are several pathways whereby these reactive species can be formed, involving the organic matter and the mineral constituents of the soil. Photons absorbed by either the phenanthrene or humic substances molecules cause their excitation. Such molecules can return to the ground state dissipating energy in various ways, mostly by photophysical processes such as internal conversion, fluorescence, intersystem crossing, phosphorescence and by energy transfer to other molecules, for example, to oxygen giving singlet oxygen ( $^1O_2$ ). Oxygen in the ground (triplet) state needs at least 94  $\text{kJ mol}^{-1}$  transform it into oxygen in the singlet state ( $^1O_2$ ). Polycyclic aromatic hydrocarbons (PAH) are known to be good sensitizers for singlet oxygen formation<sup>34</sup> and humic substances has sufficient energy in its excited states to generate singlet oxygen<sup>35</sup>. These processes are described by eqns. (6) to (9):



Singlet oxygen can attack phenanthrene molecules in the ground state which mainly causes formation of peroxides (endoperoxides) and hydroperoxides and these compounds in turn initiate radical reactions leading to further degradation of phenanthrene on the soil surfaces.

As shown in Tables 1 and 2, the experimental soil samples have significant amounts of both organic matter and semi-conducting metal oxides ( $Fe_2O_3$ , *etc.*). Under illumination with UV light, these compounds, along with phenanthrene can result in the generation of electrons. Subsequently, the superoxide radical anion ( $O_2^{\bullet-}$ ) forms because the photogenerated electrons are trapped by oxygen eqn. (10). The hydroxyl radicals and hydroperoxide radicals ( $OOH^{\bullet}$ ) are products from the reactions of superoxide radical anion with water in soil eqns. (11) to (13):



The free radicals (superoxide radical anion ( $O_2^{\bullet-}$ ), hydroxyl radicals ( $HO^{\bullet}$ ) and hydroperoxide radicals ( $HOO^{\bullet}$ ) could react directly with phenanthrene, leading to further degradation of the phenanthrene on the soil surfaces.

## Conclusion

The photolysis of phenanthrene on soil surfaces in the presence of oxygen followed pseudo-first-order kinetics. The degradation of phenanthrene is affected by the concentration of organic matter, oxygen, soil moisture and soil salinity. The organic matter enhanced the degradation of phenanthrene through energy transfer. The oxygen and soil moisture enhanced the degradation of phenanthrene through the effects of reactive oxygen (free radical and singlet oxygen). The soil salinity clearly depressed the degradation of phenanthrene through reduce the concentration of singlet oxygen ( $^1\text{O}_2$ ). The possible mechanisms of photolysis of phenanthrene on soil surfaces are discussed and it is concluded that several competing mechanisms may be responsible, including direct photolysis, photosensitized reactions and photooxidation. Photooxidation was the result of formation of free radical (superoxide radical anion, hydroxyl radicals) and singlet oxygen.

## ACKNOWLEDGEMENTS

This work is supported by National Nature Science Foundation under Grant 71021061, 2012ZX07505-002, the National Science Foundation for Young Scholars of China (No. 41101474) and National Science Foundation of China (No. 41201310).

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