



Formation of environmentally persistent free radicals during the transformation of anthracene in different soils: Roles of soil characteristics and ambient conditions

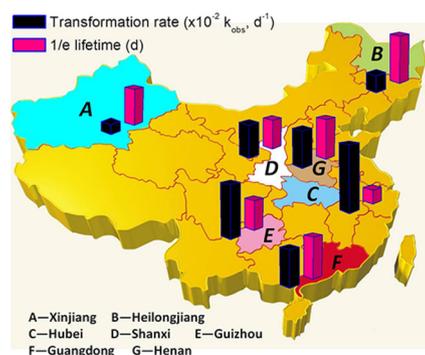


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GRAPHICAL ABSTRACT



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ABSTRACT

Transformation of PAHs, i.e., anthracene, and production of environmentally persistent free radicals (EPFRs) on seven types of representative soils were investigated, focusing on the influences of soil characteristics and ambient conditions on these reactions. The transformation rate of anthracene exhibits the order of red earth > yellow earth > latosol ~ fluvo-aquic soil > brown earth > chernozem > calcic brown soil, which is positively correlated with Fe content in soils. Afterwards, batch reactions on pure representatives of soil minerals, including Fe_2O_3 , Fe_3O_4 , FeOOH , and MnO_2 , demonstrate that anthracene is prone to mineral-promoted transformation. The presence of higher amount of organic carbon lower the transformation rate of anthracene, whereas the formed EPFRs can be stabilized for a longer time. Subsequent experiments associated with the influences of environmental conditions on mineral-promoted reactions suggest that both anthracene transformation and EPFRs generation readily occur under dry condition. Light irradiation not only promotes the formation of EPFRs, but also greatly accelerates the decay of EPFRs and the 1/e lifetime decreases from 5 to 20 d in dark to approximately 1 d. Meanwhile, the anoxic condition is favorable for the persistence of EPFRs. The obtained results suggested the potential environmental risks association with EPFRs in PAHs-contaminated soils.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), mostly discharged by anthropogenic activities such as exploitation and utilization of fossil fuels, have been widely detected in natural environment [1,2]. Particularly, soil and sediment are considered as the crucial sinks and potential reemission sources of PAHs [3]. At superfund sites associated with former coke production, coal mining, and gas works, the total PAH concentrations range from hundreds to thousands of mg kg^{-1} [4–6]. Due to their persistence, bioaccumulation, and toxicity, increased human health risk was caused by the exposure via ingestion of soil or/and inhalation of floating dust directly [7–9]. Therefore, the eco-toxicological effects of PAH-contaminated soils have been paid more attentions among the public, decision-makers and scientists [10].

Detoxification and ecological impacts of PAHs correlate with their natural attenuation processes including biotic and abiotic degradation [11,12]. Biological degradation has long been recognized as a dominant way for their disappearance in soil [13,14]. However, relatively high concentration of PAHs in contaminated sites exhibits toxicity on biomass, and thus preventing or slowing their bio-transformation [15]. Recently, lines of evidence shows that the mineral-promoted reaction, referred as abiotic transformation, can also represent a critical determinant for the fate of PAHs in soil [16–18]. As an example, clay minerals can induce chemical oxidation of PAHs via single-electron-transfer process in soil [18]. Meanwhile, the presence of metal oxides enhances the photodegradation of PAHs on upper layers [19,20]. Oxidation or polymerization of PAHs always occurs during their interaction with minerals containing Mn, Fe, and other transition metals [21–23]. The mineral-mediated transformation might involve in the electron transfer from organic compounds to electron-deficient sites, inducing the production of intermediate radicals [24,25]. Generally, free organic radicals are highly reactive and readily react with available

electron-accepting species, such as O_2 , H_2O , and parent compounds, resulting in final products by coupling, deprotonation, or abstraction termination [21,26]. Under certain conditions, however, the formed free radicals can be stabilized on mineral surfaces, generating novel, sometimes unexpected intermediate products, i.e., environmentally persistent free radicals (EPFRs), which have been considered as emerging contaminants due to their detrimental effects on human health [27,28].

Recently, the PAH-type EPFRs were observed in soil samples collected from former coking sites [29]. The spin densities in those samples correlated with the level of PAHs, transition metals, and organic carbons [29]. Several studies have been carried out to explore the role of metal oxide/ions in the PAHs transformation on mineral surfaces [28,30]. Progress has been made to understand the potential mechanism of EPFRs formation during the interaction between PAHs and individual metal/silica mineral surfaces [28]. Comparatively, only limited studies have been performed examining the PAHs transformation and EPFRs formation on whole soil with multiple metal oxide and mineral mixtures. In addition, the effect of ambient conditions on the production of free organic radicals in PAHs-contaminated soil is still poorly understood, and this information is vital to evaluate the potential risks for PAH-polluted soils with various properties.

In this study, the potential formation of EPFRs was examined during the abiotic transformation of PAHs in sterilized seven model soils obtained around China representing a broad spectrum of soil properties. Anthracene, one of the most widespread PAHs in natural phases, was selected as the target pollutant since our previous study revealed that EPFRs were readily generated during the abiotic transformation of anthracene on mineral surfaces [28]. The correlations between EPFRs production and soil properties were measured to seek the parameters influencing PAHs transformation. Role of environmental factors on the persistence of EPFRs was comprehended by tracing the evolution of



Fig. 1. Profile of the sampling sites.

spin densities over several months-time periods under dry/wet, anoxic/oxic, and light irradiation conditions. The obtained information can be of significance in seeking the vital soil composition and factors controlling the reactivity of PAHs transformation and EPFRs stability in soils. The overall results might also be applied to predict the occurrence and fate of PAH-type EPFRs in soils, thereby improving our understanding about the potential risks in contaminated sites associated with PAHs.

2. Materials and methods

2.1. Soil sampling and characteristics

Seven types of soils differing in a range of physicochemical properties were selected as the model phases. The calcic brown soil (Sample A) was obtained from Xinjiang, northwest China, possessing sandy clay loam texture and dark grayish brown color (Fig. 1). Chernozem, a black-colored soil, was sampled from a field at northeast of China (Sample B). Red earth, referred as Sample C, was taken from a site of paddy land in Hubei province, south-central China. The brown soil (Sample D), obtained from forest soil in central of Shaanxi province. Yellow earth (Sample E) obtained from Guizhou province, southwest of China. Latosol, referred as Sample F, obtained from Guangdong province. Sample G, obtained from Henan province, central of China, was identified as fluvo-aquic soil. The soil components and properties were analyzed systematically. Details of the methods are provided in Text S1 (Supporting information). Their characteristics are displayed in Table 1. The phase information of clay fraction was characterized by X-ray diffraction (XRD) technique, which was described in Text S2. Hematite (Fe_2O_3 , 99.8%), goethite (FeOOH , 99%), magnetite (Fe_3O_4 , 95%), and manganese bioxide (MnO_2 , 99%) were obtained from Shanghai Titan Scientific Co., Ltd (China).

2.2. Reaction systems of anthracene-contaminated soils

Before spiking with anthracene, soil samples were firstly sterilized following the method reported previously [31], and then oven-dried at 105 °C and transferred into a desiccator for cooling. To prepare anthracene-contaminated soils with 0.1 mg anthracene/g soil, anthracene dissolved in 2 ml of acetone was added into 1 g of individual soil, and mixed to make sure the uniform distribution of anthracene in soil. After that, the spiked samples were placed in fuming hood for 1 h to allow the solvent acetone evaporating under dark.

Batch reaction experiments were conducted in a petri dish at 25 °C following the protocol described previously [18]. Specifically, the petri dishes containing spiked soils were placed into desiccators controlling the desired temperature and relative humidity (RH) of ~ 30% unless

special statement. At pre-selected intervals, certain amount of sample was sacrificed and the residual PAHs and its intermediate products were extracted by mixture of 7 ml dichloromethane and 7 ml acetone in ultrasonic device for 30 min [32]. Afterwards, the suspensions were centrifuged, and the supernatants were filtered by a 0.22 μm syringe filter. The filtrates were analyzed by high performance liquid chromatography (HPLC) and gas chromatography-mass spectrometer (GC-MS) following the methods reported previously [33]. Instrument and operating parameters are detailed in Text S3. Blank experiments (soils without anthracene) and control experiments (anthracene-spiked silica powder) were also performed under the same reaction conditions. Silica powder (Sigma-Aldrich, acid purified sand, 325 mesh size), recognized as the most common constituent of soil, was applied in control experiment because of its inactivity for redox reaction. Each experiment was repeated 3 times.

2.3. EPR measurement

To quantify the spin densities of the original and reacted soils, 0.2 g soil sample was put into a EPR tube and measured using EMXmicro EPR spectrometer (Karlsruhe, Germany). More details of collecting spectra were provided in Text S4.

2.4. Effect of environmental conditions

To investigate the influence of ambient factors in EPFRs formation and stabilization, the spiked soil samples were aged under different conditions (anoxic, oxic, light irradiation, and high RH). For the experimental set-up in oxic condition with various RH, samples were placed inside brownish desiccators to avoid light irradiation. The RH values of reaction cells were controlled by various saturated salt solutions. For the reaction systems without O_2 molecule, soil samples were aged in anoxic glovebox. To investigate the effect of light irradiation, the soil samples were placed under simulated visible light of $\lambda > 380 \text{ nm}$ as described previously [17]. At a pre-selected time, certain amount of soil samples were sacrificed and analyzed by EPR and HPLC immediately, as described above.

3. Results and discussion

3.1. Anthracene decay in various soils

Fig. 2a displays the decays of anthracene as function of reaction time on various types of soils under oxic condition with RH of ~ 30%. Decays of anthracene occur spontaneously in days. Noted that anthracene decay rate depends on the type of soil. Among the tested seven soils, the transformation of anthracene in red earth is faster than that in

Table 1
Physical and chemical characteristics of the sampled soils.

Soil characteristic	Soil sample						
	A	B	C	D	E	F	G
Soil type	Calcic brown soil	Chernozem	Red earth	Brown earth	Yellow earth	Latosol	Fluvo-aquic soil
Location	Xinjiang	Heilongjiang	Hubei	Shaanxi	Guizhou	Guangdong	Henan
Sand, wt %	61	10.8	8.1	25.6	19.7	9.1	40.9
Slit, wt %	23.2	53.8	40.8	40.8	48.2	24.5	42.3
Clay, wt %	8.6	29.2	45.2	29.6	32.4	48.4	16.2
Total Fe, g/kg	3.4	9.2	25.2	11.7	19.1	22.6	7.3
Total Mn, g/kg	0.5	0.7	1.1	0.9	0.8	0.7	0.4
TOC, wt %	0.89	3.7	0.69	1.15	1.2	1.9	1.52
CEC, cmol/kg	12.1	36.1	12.5	14.7	10.5	10.4	9.3
pH	8.4	6.3	4.8	6.5	4.2	4.6	8.3
Surface area, m^2/g	4.6	10.9	19.2	17.9	18.6	22.1	8.5
Clay type	Montmorillonite; Vermiculite	Smectite	Kaolinite	Muscovite; Vermiculite	Montmorillonite; Vermiculite; illite	Montmorillonite; Kaolinite	Montmorillonite;Hydromica

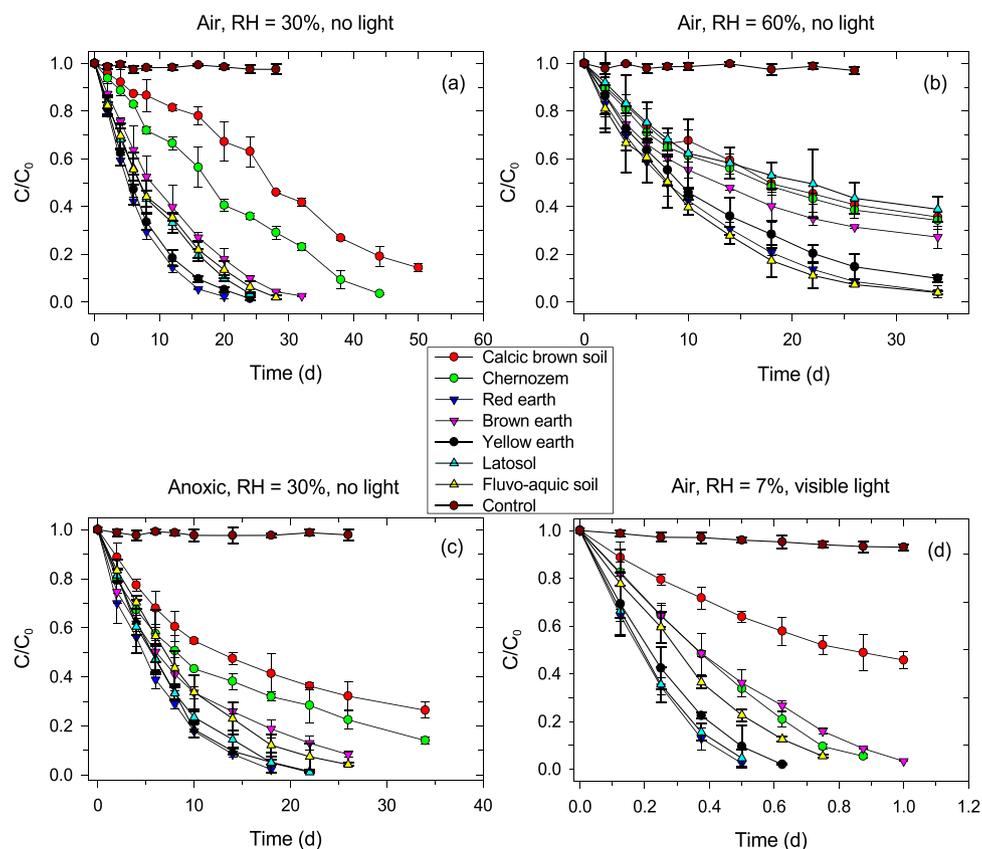


Fig. 2. The evolution of anthracene as a function of reaction time on various soils under (a) oxic (with RH of ~ 30%), (b) oxic (with RH of ~ 60%), (c) anoxic (with RH of ~ 0%), and (d) visible-light irradiation. Results from sand controls are shown as solid black symbols.

Table 2

Transformation rate constant (k_{obs}) of anthracene on various soils under different reaction conditions.

Reaction condition			First-order rate constants (k_{obs} , d^{-1})						
Atmosphere	Relative humidity	light	Calcic brown soil	Chernozem	Red earth	Brown earth	Yellow earth	Latosol	Fluvo-aquic soil
Oxic	30%	None	0.038	0.066	0.253	0.127	0.208	0.147	0.144
Oxic	60%	None	0.031	0.031	0.093	0.035	0.069	0.028	0.098
Anoxic	~0%	None	0.046	0.062	0.266	0.132	0.189	0.161	0.123
Oxic	30%	Visible light	0.758	3.322	7.364	3.161	5.977	6.082	3.861

others. Approximately 99% of the initially added anthracene is transformed within 20 d in the red earth, whereas only 33%, 59%, 82%, 95%, 90%, and 87% of anthracene is degraded on calcic brown soil, chernozem, brown earth, yellow earth, latosol, and fluvo-aquic soil, respectively. Control experiment was conducted using silica powder rather than soil, and no significant decay of PAHs ($< 3\%$) is observed during the reaction time period, implying that volatilization therein were negligible. The decay of anthracene can be described by pseudo-first-order kinetics. As shown in Table 2, under oxic condition with RH of ~ 30%, the transformation rate constant of anthracene on various soil samples follows the order of red earth > yellow earth > latosol ~ fluvo-aquic soil > brown earth > chernozem > calcic brown soil.

As described above, the tested soils were initially sterilized, suggesting that the transformation of anthracene via microbial process can be ignored in the present reaction systems. Therefore the abiotic transformation, especially mineral-promoted surface reactions such as chemical oxidation, should be responsible for the disappearance of anthracene under dark conditions [18]. The chemical oxidation is mediated by underlying soil organic or/and inorganic phases, such as iron oxides, manganese oxides, clay minerals, and humic substances [34–36]. Contents of soil components in different soils are provided in

Table 1. Soil samples, such as red earth, yellow earth, and latosol, possess higher amount of Fe species and clay minerals than other textures (Table 1). Levels of Mn vary insignificantly in various soils. While chernozem has the highest OC content among the tested soils, followed by latosol and fluvo-aquic soils. Other soil characteristics, such as CEC, surface area, and pH, show some variation on the different soils, which can be attributed to the varying of the soil components. Correlation analyses of the transformation rate of anthracene with soil components or other characteristics are presented in Fig. 3. The transformation rate is related positively to the Fe contents of soil samples ($r^2 = 0.71$), followed by decreasing correlations with Mn ($r^2 = 0.47$) and clay content ($r^2 = 0.43$) (Figs. 3a, c, and d). In addition, insignificant correlations were observed for other soil minerals such as sand and silt ($r^2 < 0.30$).

To probe the effect of soil minerals on anthracene transformation, the phase information of soil mineral was characterized by XRD. As shown in Fig. S1, the isolated clay fractions from soil samples are mainly constituted of SiO_2 , FeOOH , Fe_2O_3 , and Fe_3O_4 , MnO_2 , and clay minerals. It is noted that the relative intensities of Fe_xO_y in red earth is higher than that in other tested soils, which is in agreement with the difference in total Fe contents for various soils. The evolution of anthracene as functional of reaction time on these representative

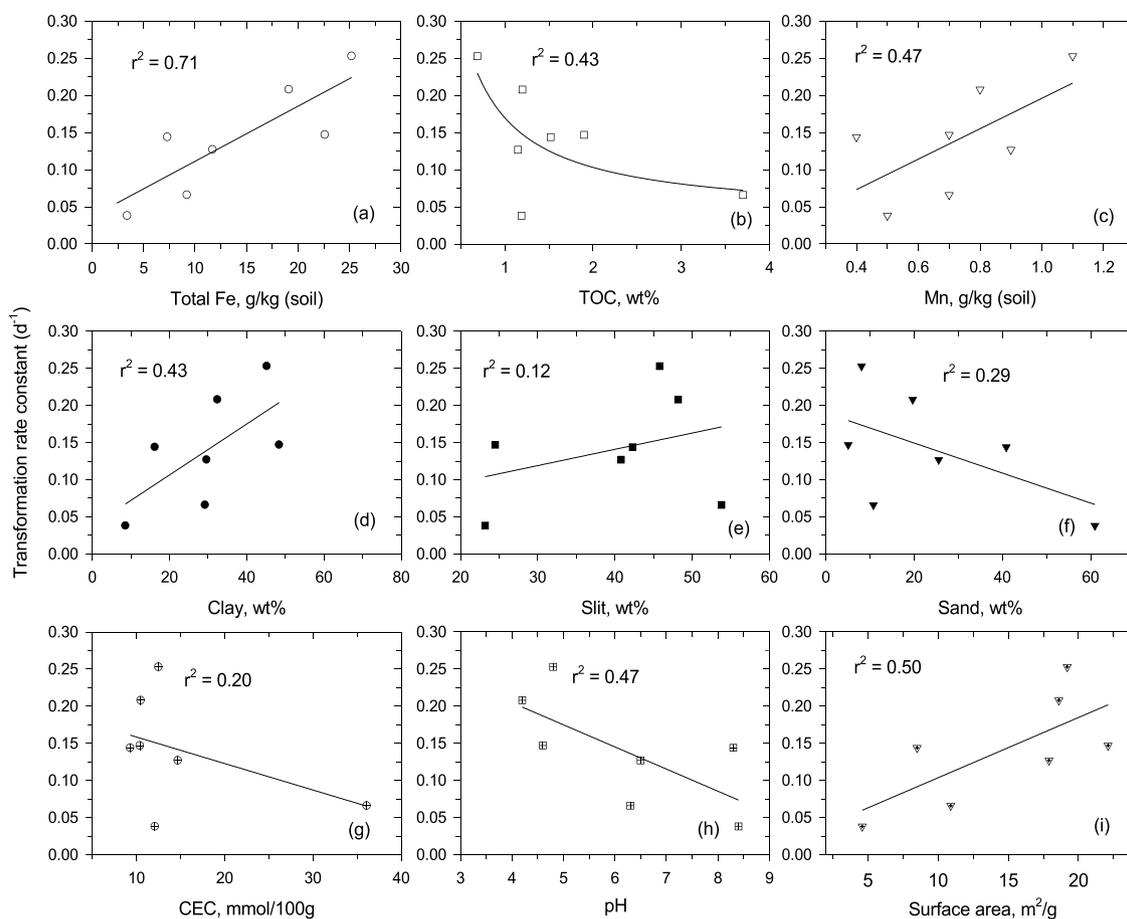


Fig. 3. Variation of transformation rate constants with contents of total Fe (a), organic carbon (b), Mn (c), clay (d), slit (e), sand (f), and CEC value (g), pH (h), and surface area (i) of the tested soils.

minerals, such as FeOOH , Fe_2O_3 , Fe_3O_4 , and MnO_2 , was investigated. As shown in Figure S2, anthracene transformation on Fe_2O_3 exhibits the highest rate among the tested minerals, followed by MnO_2 , Fe_3O_4 , and FeOOH . Meanwhile, the transformation rate on Fe_2O_3 is higher than that in soils, include red earth. These results further suggest that metal oxides, especially Fe_2O_3 and MnO_2 , play a primary role on the transformation of anthracene in the soil matrices. As reported previously, abiotic degradation of organic contaminants by reactive metal oxides such as $\gamma\text{-Fe}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-FeOOH}$, MnO_2 , and other Fe- or Mn-containing minerals has been observed in both laboratory and field studies [37–39]. These metal oxides can act as underlying catalysts or oxidants, promoting the transformation of organic contaminants via hydrolysis, nucleophilic addition, or single-electron-transfer reaction [38,39]. For PAHs, delocalized π electrons are rich and thus readily interact with electron-accepting sites, i.e., the Lewis acid, on soil minerals [32,40–43]. The coordination of PAHs to electron-deficient metal oxide/ions increases their electrophilicity, leading to a charge-transfer (CT) complex [44]. For PAHs-metal complexes with large and negative interaction energies, the CT complex may undergo ion-pair or radical-pair collapse followed by electron and proton loss. This process might lead to the formation of radical cation and further hydroxylation of radical intermediates via the reaction between carbon center of anthracene and H_2O or OH^- , inducing the oxidation of anthracene and formation of anthraquinone [41,45–47].

Soil organic matter also plays crucial roles in the fate of PAHs in soils. As displayed in Tables 1 and 2, the transformation rate of anthracene in chernozem is lower than calcic brown soil even their Fe content is equivalent. Similar phenomenon was also observed on latosol versus red soil. Overall, a weakly negative correlation between transformation rate constant and OC contents is observed in Fig. 3b.

Potential explanation for the relationship is that mineral-promoted transformation readily occurs in relatively low OC-containing soils [48]. In general, hydrophobic compounds, such as PAHs, are readily and/or frequently adsorbed to the organic phase [49]. The sequestration by OC seems to play a protective role for PAHs, ultimately inhibiting their interaction with underlying mineral interfaces [50]. In contrast, soils with low OC, such as yellow earth and brown earth, allow reactive sites on mineral surfaces available for anthracene to access, inducing its rapid transformation [51]. It is worth emphasizing that soil organic matter always wraps or complex with other solid clay/mineral components rather than exist individually. The organic contaminants, firstly adsorbed onto the organic layer-coating minerals, must then diffuse to the surface of the underlying inorganic phase, which slows down rather than totally impedes the transformation of organic contaminants [18].

In addition, correlation analyses of the transformation rate constant with other soil physicochemical properties, such as pH, CEC, and surface area, are presented in Fig. 3g–i. Relatively lower pH can induce higher rate constants, while the surface area of soils plays a positive role in the degradation of anthracene in various soil samples. These soil physicochemical properties might not influence the transformation of organic contaminants directly. However, the variation of soil properties, such as CEC and surface area, associates with the variation in the content of soil components. Low pH is always accompanied by high Fe content, which associates with high PAHs transformation rate (Table 1). Meanwhile, low pH can activate Fe oxides to active species, such as Fe ion or complexes with other soil components, favoring the transformation of organic contaminants. For the soil samples with high surface area, relatively high content of clay and low content of sand were observed, suggesting that more active components such as metal oxides and clay minerals present in soil. Therefore, the positive correlation was

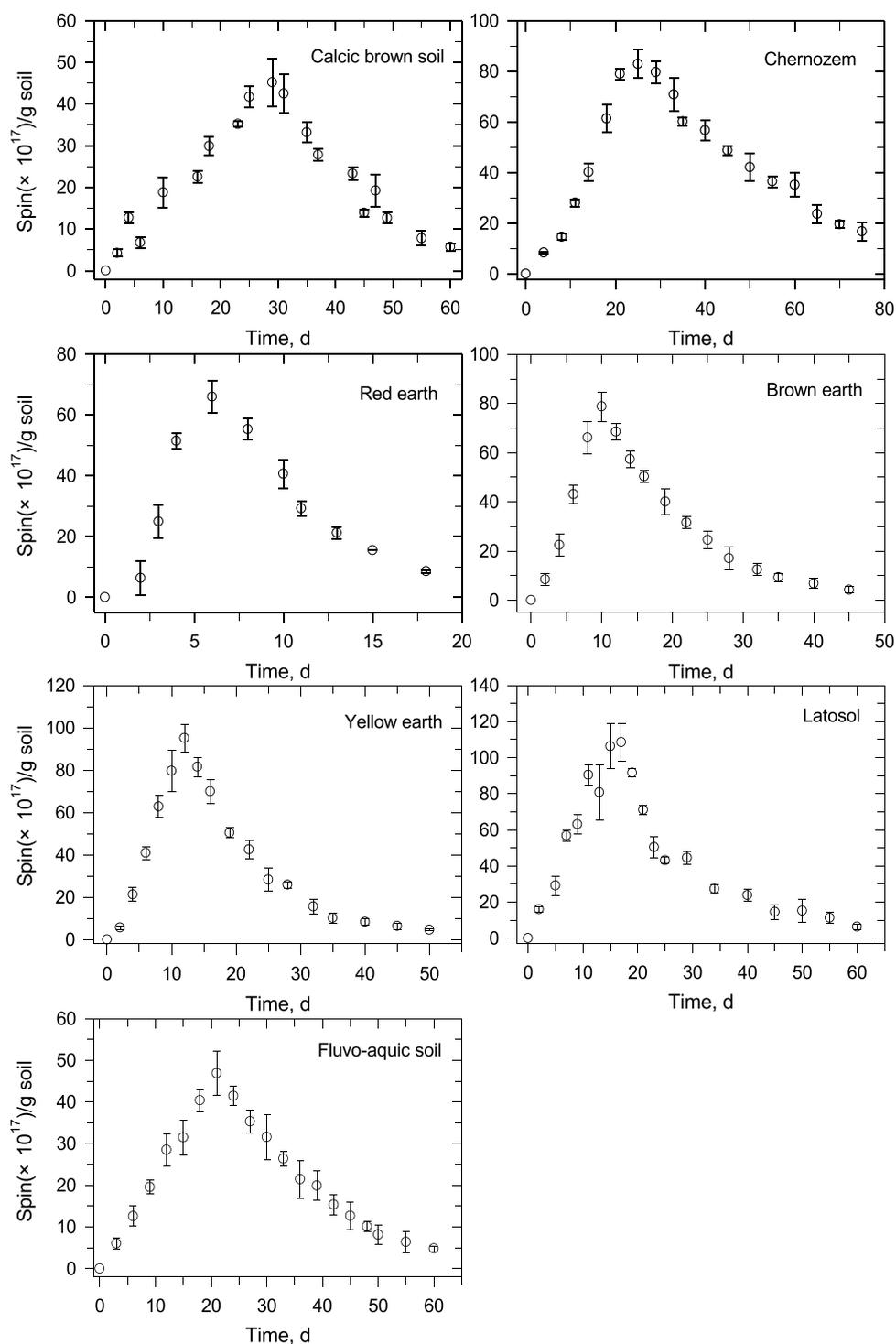


Fig. 4. Development of spin densities as a function of aging time in various soils under oxidic condition with RH of ~ 30%.

also observed between transformation rate and surface area value.

3.2. Formation and fate of EPFRs in various soils

As discussed above, anthracene transformation on soil samples might be accompanied by the formation of EPFRs. As shown in Fig. 4, the spin densities of EPFRs initially increase with the elapsed reaction time, and then gradually decrease with the further increasing in reaction time in the tested seven soils. The highest yields of EPFRs were observed in 29 d, 25 d, 6 d, 17 d, 12 d, 10 d, and 21 d on calcic brown soil, chernozem, red earth, brown earth, yellow earth, latosol, and

fluvo-aquic soil, respectively. Overall, the formation of EPFRs proceeds more rapidly on red earth, latosol, and yellow earth, followed by brown earth, fluvo-aquic soil, chernozem, and calcic brown soil. This order positively correlates with the transformation rate of anthracene on various soils (Table 2). The obtained results indicate that rapid transformation of PAHs promotes the formation of EPFRs to their maximum amounts in relatively short reaction time.

As compared to the formation rate, the maximum yields of EPFRs exhibit different trends, following the order of latosol > yellow earth ~ chernozem > brown earth ~ red earth > fluvo-aquic soil ~ calcic brown soil (Fig. 4). The free organic radicals might be more readily

Table 3

The calculated 1/e lifetimes of the produced EPFRs during the transformation of anthracene on various soils under different conditions.

Reaction condition			1/e lifetime (d)						
Atmosphere	Relative humidity	light	Calcic brown soil	Chernozem	Red earth	Brown earth	Yellow earth	Latosol	Fluvo-aquic soil
Oxic	30%	None	14.75	19.39	5.77	11.81	12.13	17.27	16.92
Oxic	60%	None	12.45	11.96	3.26	7.72	8.58	10.46	13.5
Anoxic	30%	None	15.43	19.59	6.84	10.94	14.40	19.58	16.34
Oxic	30%	Visible light	1.03	1.83	0.42	0.89	0.51	0.58	1.27

produced and accumulated in latosol, chernozem, and yellow earth than that in other soils. Interestingly, the maximum yield of EPFRs in red earth is lower than most of tested soil samples, especially latosol. The yields or accumulation of EPFRs are determined by not only the formation rate but also their stabilization on soils. The stabilization of EPFRs in soils can be characterized by their decay rates. EPFRs decays from their maximum yields are fitted by pseudo-first-order model, and their 1/e lifetime is utilized to assess their stabilization in various soils (Fig. S3). As shown in Table 3, the stabilization of the EPFRs produced in different soils follows the order of chernozem > latosol ~ fluvo-aquic soil > calcic brown soil > yellow earth ~ brown earth > red earth. The free organic radicals in red earth exhibit a relatively “fast” decay with 1/e lifetime of 5.7 d. While the free organic radicals on chernozem produced slowly, however, the radicals are relatively stabilized once formed, resulting in the longest lifetime compared with other soils.

The variation of lifetime of EPFRs in different soils can be understood by seeking their relationship with soil components. As shown in Fig. 5a, the 1/e lifetime has a weakly negative relationship with Fe content in soils (Fig. 5a). The presence of Fe not only promotes the formation of EPFRs, but also accelerates their decomposition to final products. Meanwhile, the 1/e lifetime is positively correlated with the amount of OC in soil, indicating that soil organic matter play a vital role in the persistence of EPFRs. As reported previously, elemental carbon and humic substances might also act as matrices for free radicals, and thus the produced EPFRs can be sequestered by OC to avoid or delay the rapid decomposition [52]. In addition, 1/e lifetime is uncorrelated to clay content, Mn content, and other soil parameters such as pH, surface area, and CEC (Data not showing). These results indicate that EPFRs are readily produced and stabilized on the interfaces between iron minerals and organic matters [53]. Overall, the accumulation of EPFRs correlates with the transformation rate of their precursors and the stabilization of the produced radical intermediates.

3.3. Effects of environmental conditions

PAHs transformation and EPFRs formation are not only affected by

soil characteristics but also the environmental conditions or/and locations [29]. To evaluate the persistence of EPFRs under various conditions, such as soil surface layer with light-irradiation, deep soil with deficiency of O₂ and light, and moist or dry ambient with various H₂O contents, the evolutions of anthracene and EPFRs as functions of reaction time in various soil samples are monitored accordingly.

3.3.1. Oxic condition with RH of 60%

PAHs transformation and EPFRs formation highly depend on the RH in the reaction ambient. When RH is ~ 60%, in this study, the transformation of anthracene is significantly retarded (Fig. 2b). Compared with that in relatively dry condition (RH of ~ 30%), the transformation rate constants of anthracene decrease by 18%, 53%, 66%, 72%, 67%, 81%, and 32% in calcic brown soil, chernozem, red earth, brown earth, yellow earth, latosol, and fluvo-aquic soil, respectively, which was not be observed in control sample. It is noted that the soil matrices, such as red earth, brown earth, and yellow earth, with high amount of clay and Fe minerals induce more inhibiting effect than others. Similar phenomenon was also observed in previous work, in which the addition of water resulted in a rapid decay of reaction rate during the transformation of arene on mineral surfaces [54].

In dry soils with low OC content, distribution of non-polar organics, such as PAHs, mainly dominated by their interaction with surface sites of inorganic minerals, particularly clays [55]. However, these reactive sites or cations on mineral surfaces are likely to be hydrated under high RH condition, leading to the generation of water layer on mineral surfaces [56,57]. The coverage of water molecules induces the detachment of organic compounds, such as anthracene, from the coordination sites, like Lewis acid sites [58]. The weakened interaction between anthracene and active sites decreases the possibility of electron transfer reaction [26]. Therefore, higher RH induces lower transformation rate of anthracene in soils [17,59].

The presence of high amount of H₂O also influences the formation of EPFRs [26]. As shown in Fig. S4a, both the formation rate and the highest yield of EPFRs in red earth are inhibited under relatively high RH value (~ 60%). As reported previously, PAH-type radical cations readily react with H₂O, resulting in their rapid decay on mineral

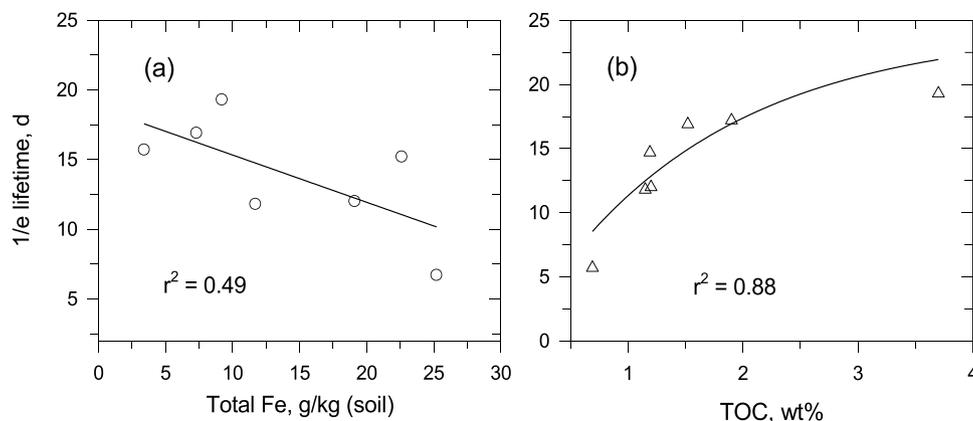


Fig. 5. Variation of 1/e lifetime with contents of total Fe (a), and organic carbon (d) in various soils.

surfaces [28]. The high water content thus inhibits the accumulation of EPFRs. Table 3 presents the lifetimes of the observed EPFRs in various soil samples under RH of 60%. Compared with their 1/e lifetimes under relatively dry condition (RH of ~ 30%), the produced EPFRs more readily decay in red earth and chernozem than that in calcic brown soil and fluvo-aquic soil. This also be attributed to the difference of soil components. Red earth and chernozem possess relatively higher amount of clay or/and OC than calcic brown soil and fluvo-aquic soil (Table 1). As discussed above, the clay minerals and OC are structurally hydrophilic and readily absorb H₂O to promote the quenching of EPFRs. Overall, high RH not only inhibits the formation rate of free radicals, but also quenches the produced EPFRs.

3.3.2. Anoxic condition

Storage of anthracene-contaminated soils in anoxic glovebox enables an estimation of the PAHs transformation and production of EPFRs under anoxic condition, featuring the redox circumstances in deep soil, where O₂ deficiency prevails. Interestingly, the absence of oxygen insignificantly influences the decay rate for all the tested soils compared to that under air condition (Fig. 2c and Table 3). The result suggests that oxygen molecules merely influence the transformation of anthracene on soils. Meanwhile, evolved spin densities are monitored for all the tested soils. As shown in Fig. S4b, in red earth, two time periods of EPFRs evolution appear; a gradually increase followed by a relatively slower decay. The increase of EPFRs under anoxic condition can be attributed to the reaction between anthracene and residual H₂O molecules in soil samples, inducing the formation of EPFRs, such as oxygenic carbon-centered radicals [18]. Once produced, the EPFRs can be persistent for a relatively long period under anoxic condition.

3.3.3. Light condition

On dry and sunlight-exposed soil surface, transformation of organic contaminants may be dominated by photolysis pathway [60]. In the present study, anthracene transformation and EPFRs formation are investigated by aging the soil samples under simulated visible-light irradiation. The evolution of anthracene as a function of reaction time is presented in Fig. 2d. Under visible light irradiation, the transformation rate of anthracene is significantly increased. More than 50% of spiked anthracene can be transformed in hours. The relevant photodegradation rate follows the order of red earth > Latosol ~ Fluvo-aquic soil > Yellow earth > chernozem ~ brown soil > calcic brown soil, which is inconsistent with anthracene transformation without irradiation. As shown in Table 2, the transformation rate constants are 20×, 50×, 30×, 24×, 31×, 41× and 26× higher than that under dark conditions on calcic brown soil, chernozem, red earth, brown earth, yellow earth, latosol, and fluvo-aquic soil, respectively. Noted that the enhancement of photo-transformation rate on chernozem, red earth, yellow earth, and latosol is greater than the corresponding variations on calcic brown soil and brown soil. That also be due to the difference in soil components. For control experiments performed with silica powders, the decay of anthracene is less than 5% during a 24 h time period (Fig. 2d), suggesting that the photo-transformation of anthracene occur mainly due to the soil active components, such as metal oxides, clay minerals, and organic matter.

As reported previously, inorganic minerals and soil organic matter can promote the photodegradation of organic pollutants in soils [61,62]. During the photodegradation process, iron minerals, such as iron oxides and Fe-associated clays, act as a photo-catalyst, which induce the generation of reactive oxygen species (ROS) in soils without H₂O₂ addition [32]. These produced ROS can degrade or mineralize organic compounds rapidly. On the other hand, soil organic matter possesses notable visible-light absorption ability, and then transfers into its excited states, such as SOM* [63]. The excited SOM might react with organic contaminants (i.e. anthracene) directly, induce the formation of intermediate radicals or final products in soil. Meanwhile, the excited SOM also reduces molecular oxygen, forming singlet oxygen (¹O₂) and

other ROS, which can enhance the photodegradation rate of organic contaminants [64].

Both of EPFRs formation and stabilization are influenced by the light irradiation. As shown in Fig. S4c, light irradiation of red earth leads to more than a 10-folds increase of the highest yields of EPFRs than that in dark condition. Meanwhile, the highest yield of EPFRs is observed in ~ 0.3 d of reaction time. The results suggest that light irradiation accelerates the formation of EPFRs in soil. The enhanced formation of free organic radicals can be attributed to the photo-enhanced electron-transfer between organic contaminants and soil minerals or/and photosensitized properties of soil components [65]. Compared with the reaction without light irradiation, the photo-mediated EPFRs decay to undetectable level rapidly in ~ 0.7 d of reaction time (Fig. S4). The 1/e lifetimes of produced EPFRs on various soil samples are presented in Table 3. The light irradiation results in a significant decrease in 1/e lifetime of EPFRs. Therefore, light irradiation not only accelerates the formation of EPFRs, but also promotes the decomposition of the produced free organic radicals. It is noted that the amplitude of the change is significantly higher in the yellow earth and latosol samples compared to other soil samples. As reported previously, soil active components, such as clay minerals, humic acid, and metal oxides, act as sensitizers and catalysts for the production of ROS including hydrogen peroxide, singlet oxygen, or superoxide anion [66]. These ROS readily react with intermediate radicals and induce their decomposition to final products.

4. Conclusion

This study examined the transformation of anthracene and possible formation of EPFRs in seven soils with various physicochemical properties. The obtained results suggested that PAHs transformation and EPFRs formation depend on the soil characteristics. Soil samples with high amount of Fe species, such as red earth, promote the transformation rate of PAHs and induce the formation of EPFRs rapidly. Inversely, PAHs transformation could be inhibited in relatively high OC-containing soils. In addition, environmental conditions, such as RH level, anoxic/oxic, and light/dark, significantly influence the formation and persistence of EPFRs in PAHs-contaminated soils. The obtained results provide the first direct evidence for PAHs transformation in various soils, supporting the plausibility of their in situ transformation in soils under environmental conditions, and demonstrate that abiotic degradation of PAHs may induce the formation of EPFRs in soils. These results also suggested that the potential environmental risks association with PAH-EPFRs should be re-evaluated based on the soil characteristics and locations.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.jhazmat.2018.08.056>.

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