Formation of environmentally persistent free radicals and reactive oxygen species during the thermal treatment of soils contaminated by polycyclic aromatic hydrocarbons

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Environmental Chemistry Letters (2020) 18:1329–1336
https://doi.org/10.1007/s10311-020-00991-1

Formation of environmentally persistent free radicals and reactive oxygen species during the thermal treatment of soils contaminated by polycyclic aromatic hydrocarbons

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Abstract
Environmentally persistent free radicals (EPFRs) are emerging contaminants of increasing concern due to their toxicity for life and ecosystems, yet their formation, behavior and fate are poorly known. In particular, there is actually no knowledge on the formation of those radicals during the thermal treatment of soils containing polycyclic aromatic hydrocarbons. Such knowledge is important because thermal treatment is a remediation method used to decontaminate soils by removing and degrading PAHs. Here, we studied the formation of radicals in three types of cultivated soils, bauxite soil, fluvo-aquic soil and chernozem soil, artificially contaminated by benzo[a]pyrene, during thermal treatment from 100 to 200 °C for 1 h, using electron paramagnetic resonance. Results show spins densities of radicals up to of 2.079×10^{17} spins/g for bauxite soil, 1.481×10^{17} spins/g for fluvo-aquic soil and 8.592×10^{16} spins/g for chernozem soil at 175 °C. The formed radicals exhibited multiple decays during their observable time and the shortest 1/e lifetimes of radicals up to 757.58 h. These findings are strengthened by EPFR-induction of reactive oxygen species (ROS), $O_2^{\cdot-}$ and $^{\cdot}OH$, which increased in concentrations from 100 to 200 °C. Overall, our results demonstrates for the first time that thermal treatment of PAHs-contaminated soils induces the formation of EPFRs and suggests that thermal treatment might not be a fully clean remediation method for soils as thermal treatment creates new contaminants.

Keywords Thermal treatment · Polycyclic aromatic hydrocarbons · Risk · Environmentally persistent free radicals · PAHs · EPFRs · ROS

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are priority pollutants of global concern because they induce teratogenic, carcinogenic and mutagenic effects on organisms (Samanta et al. 2002; Li et al. 2008). Due to their hydrophobic properties, around 90% of PAHs in the environment are ultimately deposited into soils and sediments (Eriksson et al. 2000). After entering the soil, PAHs are stable or degrade slowly due to their chemical stability and as a result of soil conditions that inhibit degradation, e.g., physical sequestration and anoxia (Lichtfouse et al. 1997; Chiou et al. 1998). Chemical oxidation (Do et al. 2009), bioremediation (Gan et al. 2009), photo-degradation (Wang et al. 2015; Jia et al. 2015a, b) and thermal treatment (Li et al. 2018) have been used to remediate soils contaminated by PAHs. Thermal treatment is widely used to decontaminate industrial soils because this method is fast and has low cost and high efficiency (Henner et al. 1997; Gan et al. 2009). For instance, soils from the two major ancient gasworks in Paris, which were heavily contaminated, have been remediated by thermal treatment, notably for the rapid construction of a major soccer stadium.

Volatilization is considered to be the main phenomenon for the removal of organic contaminants by thermal

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treatment (Gilot et al. 1997; Falciglia et al. 2011). Nonetheless, recent reports indicated that transformation of organic pollutants might occur during thermal treatment. For example, Cruz et al. (2012) found that pentachlorophenol was converted to pentachlorophenoxyl during thermal treatment, which was explained mainly by thermal oxidation. Zhang et al. (2019) also found that thermal oxidation occurred during thermal treatment of soil contaminated by catechol. Furthermore, Jia and Wang (2013) found that PAHs oxidation occurred even under natural conditions. Oxidation may involve electron transfer from organic compounds to electron-lacking sites, which may, in turn, lead to the formation of environmentally persistent free radicals (Jia et al. 2016).

Environmentally persistent free radicals (EPFRs) are emerging contaminants that are raising high concerns due to their adverse effects on human and ecological health (Pryor et al. 1983; Lomnicki et al. 2008). Currently, EPFRs have been mainly detected in cigarette tar, combustion-generated particles, atmospheric particulate matters and soil contaminated by organic pollutants (Fang et al. 2014; Wang et al. 2018). The formation of EPFRs in soil is drawing attention because soils are vast reservoirs of complex chemical pollutants such as metals and organics (Zhang et al. 2019). The presence of EPFRs in PAHs-contaminated soil was recently detected at room temperature (Jia et al. 2017). Nevertheless, to date, there is no report on the potential formation, stability and environmental effects of EPFRs during thermal treatment of PAHs-contaminated soils. Moreover, the effect of soil properties on the formation of EPFRs during thermal treatment is unknown. Such information is critical for evaluating the potential risks of thermal treatment of PAH-contaminated soils. Here, we investigated the formation of EPFRs and reactive oxygen species (ROS) during the heating of three types of soils, bauxite soil, fluvo-aquic soil and chernozem soil, spiked with benzo[a]pyrene, from 100 to 200 °C.

Materials and methods

Chemicals

Benzo[a]pyrene (98%), methanol (HPLC grade), dimethyl sulfoxide (DMSO, 99%) and high-purity 5,5-dimethyl-1-pyrroline-N-oxide (DMPO, 98%) were purchased from J&K Chemical Ltd., Beijing. Dichloromethane and acetone were of analytical grade from Sinopharm Chemical Reagent Co., Shanghai. Quartz particles in the form of acid purified sand were purchased from Kemiou Chemical Reagent Co., Tianjin.

Preparation of soils contaminated by benzo[a] pyrene

Three different cultivated soils, including bauxite soil, fluvo-aquic soil and chernozem soil, were sampled from surface of the 0–20 cm soil layer in Shaanxi, Henan and Heilongjiang provinces of China. These soils are representative soils of China; they differ in the amount of soil components such as clay mineral, organic matter and transition metals. Soil samples were air-dried for 24 h at ~ 23 °C and then sieved through 100 mesh before analysis. The soil texture, organic carbon (OC), clay and metal contents, pH and cation exchange capacity (CEC) were analyzed systemically. Benzo[a]pyrene was undetectable in the original soils. Details of the methods are provided in Text S1 (Supporting information). Results are provided in Table S1.

The preparation of benzo[a]pyrene-contaminated soils was previously described (Jia et al. 2018). Briefly, 1 g of soil sample was mixed with 1 mL of acetone solution containing 500 mg L^{-1} of benzo[a]pyrene. The soil–benzo[a] pyrene suspension was rapidly stirred for 30 min to promote the interaction between soil and benzo[a]pyrene molecules. Benzo[a]pyrene-containing soil samples were placed in the dark at about ~ 23 °C until the acetone was completely evaporated. The benzo[a]pyrene-contaminated soils were then stored at − 4 °C for subsequent experiments. The final concentration of benzo[a]pyrene in samples was in the range of 497–502 mg kg^{-1}. The samples of benzo[a]pyrene-spiked quartz particle were prepared using the same method as mentioned above.

Thermal treatment of samples contaminated by benzo[a]pyrene

Thermal treatment was performed using an experimental apparatus under a continuous flow of N_2 with a flow rate of 1 L min^{-1} (Scheme S1). The apparatus consisted of an oil bath heater (DragonLAB, MS-H-Pro + , China), a two-necked round bottom flask with soil sample loading, two porous gas washing bottles for capturing of volatile organics by a 1/1 v/v solution of acetone and dichloromethane and a round-bottomed flask filled with water to absorb exhaust gases. Before thermal treatment, the air inside the device was removed by flushing N_2 for 5 min. Then, 5 g of contaminated soil was placed in the two-necked round bottom flask, which was transferred into the oil bath and held there at the desired temperature for 1 h. After cooling down to ~23 °C, the soil was stored in sealed polyethylene bags prior to analysis. A blank experiment involved non-polluted quartz particles and uncontaminated three

cultivated soils was heated under the same conditions as above. And a control experiment involved benzo[a]pyrene-spiked quartz particles was carried out under the same conditions as mentioned above. Parallel experiments were repeated for three times.

The residual concentration of benzo[a]pyrene in soils after thermal treatment was quantified by high-performance liquid chromatography (HPLC, Thermo Fisher Scientific U3000), as described previously by Jia et al. (2018), and the specific methods are provided in Text S2.

Electron paramagnetic resonance

EPR measurements were performed at ~ 23 °C using a Bruker EMXmicro-6/1/P/L spectrometer (Karlsruhe). Specifically, 50 mg of thermally treated soil was immediately put into a 1.5 mL centrifuge tube and vortex mixed with 300 µL of acetone and dichloromethane 1/1 v/v. A syringe was used to draw a certain amount of the mixture and passed through a 0.45 µm filter. The filtrate was extracted by capillary and placed in EPR tube to detect EPFRs. For the detection of reactive oxygen species (ROS), 50 mg of thermally treated soil was suspended into 200 µL 0.1 M DMPO aqueous solution or 0.1 M DMPO in DMSO. Subsequently, the mixture was shaken for 1 min by a vortex oscillator, and the suspension was filtered through a 0.45 µm filter. Then, the filtrate was put in a capillary and placed in EPR tube for detection of reactive oxygen species (ROS). EPR instrument operating parameters are provided in Text S3.

Persistence of environmentally persistent free radicals

The persistency of EPFRs in soils after thermal treatment was detected by aging the soil samples in ~ 23 °C under dark and anaerobic environment. The detailed method is given in supplementary Text S4.

Results and discussion

Formation of environmentally persistent free radicals during soil thermal treatment at 100–200 °C

We tested the potential generation of environmentally persistent free radicals (EPFR) in thermally treated soils. The control experiment, i.e., the benzo[a]pyrene-containing quartz sample, and three types of cultivated soils, bauxite soil, fluvo-aquic soil and chernozem soil, were analyzed by electron paramagnetic resonance (EPR) after thermal treatment at 100–200 °C for 1 h.

Results show that negligible EPR signals are observed in the quartz control (Fig. 1a). This is explained partly the absence of transition metals in quartz (Table S1), since the

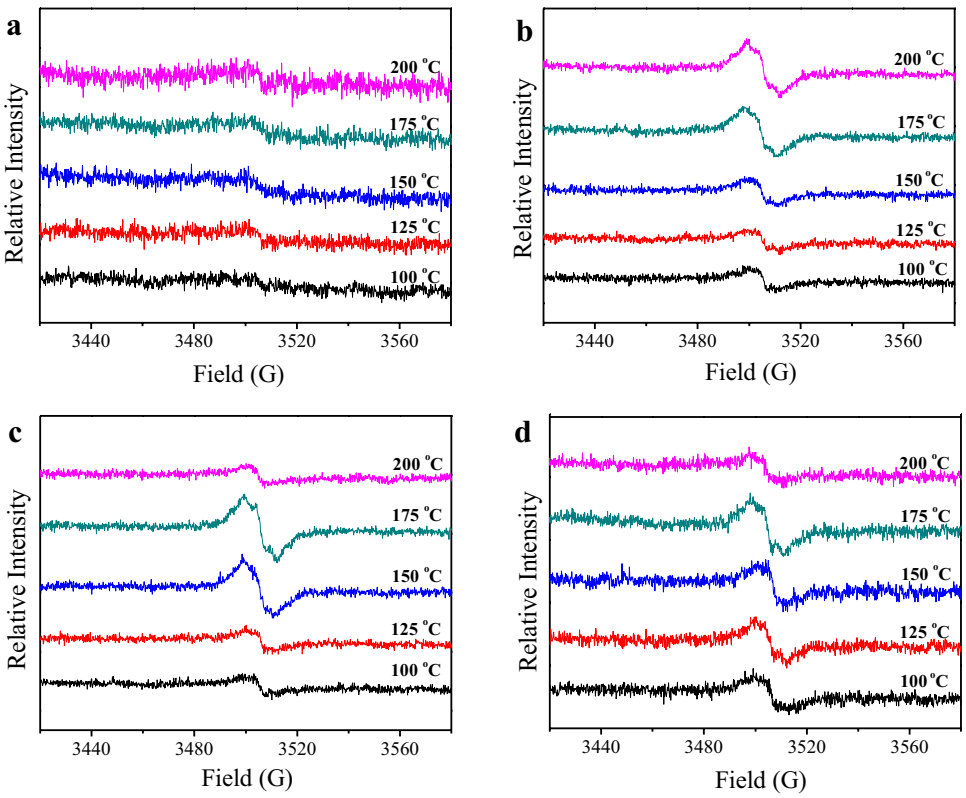

Fig. 1 Formation of environmentally persistent free radicals (EPFRs) in benzo[a]pyrene-contaminated samples of quartz particles (**a**, control), bauxite soil (**b**), fluvo-aquic soil (**c**) and chernozem soils (**d**) after 1 h of thermal treatment at 100–200 °C. Note the near absence of signal in quartz particles, meaning that soil active components were needed to produce EPFRs. Note also the increasing signal intensity with temperature up to 175 °C, meaning that radicals were formed by thermal treatment

formation of EPFRs has been shown to result from interactions between organic pollutants and transition metals (Kuzina et al. 2004; Han and Chen 2017). The interaction between aromatic compounds with transition metals, e.g., Ni and Cu, might involve the activation of aromatic compounds R–C–H, followed by H transfer from organic compounds to electron-deficient sites, thus inducing the formation of intermediate radicals (Sarkar et al. 2019; Trinh et al. 2016). The negligible EPR signals observed for quartz may be also explained by the absence of clay minerals and organic matter. Our finding agrees with our previous report showing that benzo[a]pyrene is mainly removed by volatilization in quartz sands, whereas benzo[a]pyrene is mainly removed by thermal transformation when clay minerals and organic matter are present in soils, thus generating radicals (Jia et al. 2020).

Results also show distinct signals for the three soils after thermal treatment (Fig. 1b–d). Moreover, the EPR intensity increased with temperature up to 175 °C. This finding means that EPFRs are formed by increasing the temperature. The control of radical formation both by temperature and by the presence of benzo[a]pyrene is confirmed by further control experiments showing that EPR signal is small without benzo[a]pyrene (Figs. S1 and S2).

We further identified the types of EPFRs via EPR signals characteristics such as the g-factor (Table 1). We found g-factor was 2.00280–2.00297 for the bauxite soil, 2.00294–2.00299 for the fluvo-aquic soil and 2.00269–2.00291 for the chernozem soil. These values are typical of free organic radicals. All spectra are consistent with the characteristics of benzo[a]pyrene-EPFR (Jia et al. 2018). According to previous studies, free radicals with g-factor lower than 2.0030 are considered as carbon-centered radicals; the g-factor of oxygen-centered radicals is greater than 2.0040; and free radicals with g-factors in the range of 2.0030–2.0040 are mixed radicals of carbon- and oxygen-centered radicals (Zhu et al. 2019). Here, the g-values of the EPR signals ranged from 2.0025 to 2.0030, indicating that more carbon-centered radicals were formed during the thermal treatment of benzo[a]pyrene-contaminated soils.

The range of EPFRs spins densities was 3.93×10^{16}–2.08×10^{17} spins/g for the bauxite soil, 3.29×10^{16}–1.48×10^{17} spins/g for the fluvo-aquic soil and 2.95×10^{16}–8.59×10^{16} spins/g for the chernozem soil. The spins densities of EPFRs increased in all soils from 100 to 175 °C and then decreased (Table 1). At the same time, the residual benzo[a]pyrene concentration decreased with temperature (Fig. S3). These results suggest that thermal treatment induced the transformation of benzo[a]pyrene into benzo[a]pyrene–EPFRs. This interpretation is supported by the work of Karimi-Lotfabad et al. (1996) who suggested that the EPR intensity is increased by the decomposition of benzo[a]pyrene into aromatic subunits and free organic radicals.

At 200 °C, the spins densities decreased for all soils (Table 1). These decreases could be explained by several phenomena. For instance, EPFRs may form new compound, e.g., through Eley–Rideal or Langmuir–Hinshelwood surface reactions (Lomnicki and Dellinger 2003). Alternatively, EPFRs may be thermally decomposed or stabilized by radical–radical recombination, leading to the formation of new, secondary, molecular contaminants (Maskos and Dellinger 2008).

Overall our results show that 1) thermal treatment at relatively low temperatures induces the formation of EPFR, 2) the concentration of EPFR increases up to a peak at 175 °C, and 3) the formation of EPFR involves in the interaction between benzo[a]pyrene and soil active components.

Persistence of radicals in soils

We studied the persistence of EPFR because EPFR has longer half-lives than traditional free radicals, e.g., $^{\cdot}OH$ and $O_2^{\cdot-}$. As a consequence, EPFR may exhibit toxicity risks in the long run. Figure 2 presents spins densities and spin decay rate of EPFR in the dark at room temperature, after 175 °C thermal treatment for 1 h. Results show that EPFR spin densities in the three soils decrease with time (Fig. 2a). Noteworthy, the bauxite soil displays a sharper spin density decrease versus the fluvo-aquic and chernozem soils.

Results further show that decay rates decrease from the bauxite soil, with k of 0.00538, to the chernozem soil, with k of 0.00141 (Fig. 2b). In addition, the decays of

Table 1 Electron paramagnetic resonance (EPR) of benzo[a]pyrene-contaminated cultivated soils and quartz

Temp (°C)	Bauxite soil		Fluvo-aquic soil		Chernozem soil		Quartz	
	g-factor	Spins (e^{16}/g)	g-factor	Spins (e^{16}/g)	g-factor	Spins (e^{16}/g)	g-factor	Spins (e^{16}/g)
100	2.00294 ± 0.000042	3.934 ± 0.3747	2.00299 ± 0.000051	3.842 ± 0.5382	2.00286 ± 0.000039	2.947 ± 0.2649	n.d	EDL
125	2.00297 ± 0.000037	4.950 ± 0.2318	2.00298 ± 0.000036	4.524 ± 0.5226	2.00289 ± 0.000045	4.512 ± 0.5413	n.d	EDL
150	2.00280 ± 0.000046	8.478 ± 0.5226	2.00296 ± 0.000058	12.148 ± 0.7642	2.00269 ± 0.000052	5.088 ± 0.4562	n.d	EDL
175	2.00295 ± 0.000029	20.790 ± 0.9830	2.00298 ± 0.000041	14.813 ± 0.5276	2.00290 ± 0.000034	8.592 ± 0.5347	n.d	EDL
200	2.00294 ± 0.000015	18.142 ± 0.7352	2.00294 ± 0.000037	3.286 ± 0.9137	2.00291 ± 0.000038	2.976 ± 0.1589	n.d	EDL

n.d. signifies that EPR signals were not detected; EDL means that the measured spins densities were below detection limit

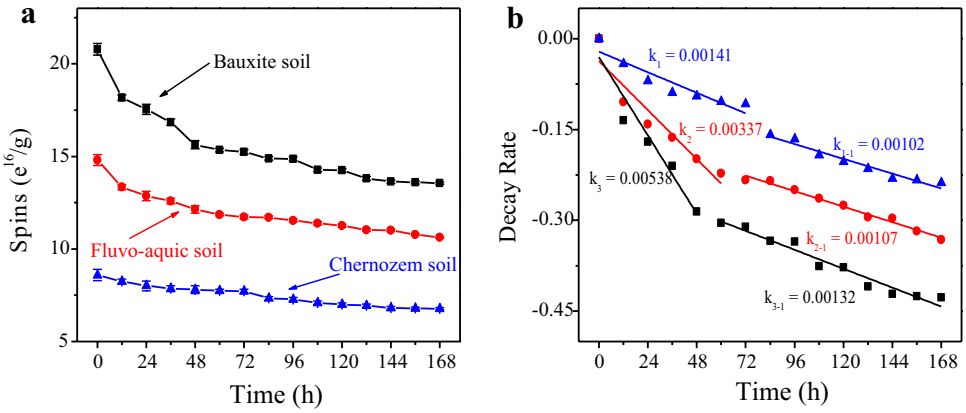

Fig. 2 **a** Variation in spin densities with reaction time and **b** decay rates of environmentally persistent radicals (EPFR) in benzo[a]pyrene-spiked bauxite soil, fluvo-aquic soil and chernozem soil, after 1 h of thermal treatment at 175 °C; $t_{1/e}$ for bauxite soil were 185.87 h and 757.58 h; $t_{1/e}$ for fluvo-aquic soil were 296.74 h and 934.58 h; $t_{1/e}$ for chernozem soil were 709.22 h and 980.39 h. The black, red and blue represent bauxite soil, fluvo-aquic soil and chernozem soil, respectively. Note the decrease of g-factor and decay rates. Note that decay evolution displays two time periods, a fast decay from 0 to 48–72 h and a slower decay thereafter. Note also the faster decay for bauxite soil

EPFRs can be split into two time periods: a rapid decrease from 0 h to about 48–72 h and then a slower decrease. This change of decay rate was more pronounced for bauxite and fluvo-aquic soils. Accordingly, 1/e lifetimes of 185.87 h were higher for the bauxite soils during the first 48 h of soil storage, versus 757.58 h from 48 to 168 h, for instance.

The overall decay can be explained by the transformation of intermediate radicals into stable compounds, according to Zhao et al. (2019). The change in decay rates after 48–72 h can be explained by the survival of the most stable aromatic radicals, as suggested by Cruz et al. (2012). This hypothesis is strengthened by the presence of at least three superimposed peaks in the resonance signals of soils just after thermal treatment (Fig. 1). The differences in decay rate evolution with time for the three soils are likely to result from the presence of organic matter. Indeed, the higher decay rate of k of 0.00538 is observed for the bauxite soil, which is the poorest in organic matter, of 0.956%w, whereas the lowest decay is observed for the chernozem soil, which is the richest in organic matter, of 2.07%. This assumption is in agreement with the stabilization of radicals by organic matter through π-stacking and hydrophobic associations, thus resulting in longer half-lives (Coates et al. 2002).

Overall, our results show that the decay of EPFRs in benzo[a]pyrene-spiked soils heated at 175 °C decreases with time in two stages, which are likely to be due to the presence of free organic radicals of various stabilities. The lowest decay observed for the chernozem soil is most probably due to the presence of organic matter that stabilizes the radicals.

Generation of reactive oxygen species

EPFRs can induce the formation of reactive oxygen species (ROS), which are considered toxic because these species cause oxidative stress on organs and cells (Ayres et al. 2008; Saravia et al. 2013). Therefore, we studied the formation of $O_2^{\cdot-}$ and $^{\cdot}OH$ in benzo[a]pyrene-spiked soils heated from 100 to 200 °C. Results show the presence of $O_2^{\cdot-}$ and $^{\cdot}OH$ in heated the bauxite soil, with typical resonances (Fig. 3a, b). $O_2^{\cdot-}$ and $^{\cdot}OH$ were also founded in the heated fluvo-aquic soil and heated chernozem soil (data not shown). In addition, the ROS were absent in control and blank experiments. These findings mean that the formation of $O_2^{\cdot-}$ and $^{\cdot}OH$ is dependent on the formation of EPFRs.

Results also show that the concentrations of $O_2^{\cdot-}$ and $^{\cdot}OH$ increased with temperature (Fig. 3c, d). This finding can be explained by the conversion of EPFRs into $O_2^{\cdot-}$ and $^{\cdot}OH$ because the concentration of EPFRs is decreasing at high temperature, in agreement with findings of Maskos and Dellinger (2008). The formation of $O_2^{\cdot-}$ could also be explained by the reduction in O_2 into $O_2^{\cdot-}$ by EPFRs as reducing agents (Khachatryan et al. 2011). Moreover, we observed that the bauxite soil produced the highest concentrations of $O_2^{\cdot-}$, whereas the chernozem soil produced the highest concentrations of $^{\cdot}OH$. This finding might be explained by the highest content in transition metals of the chernozem soil (Table S1). Indeed, as reported previously, transition metal oxides promote the formation of $^{\cdot}OH$ (Amaniampong et al. 2018, 2019; Trinh et al. 2018; Jia and Wang 2013).

Overall, our findings show an increasing formation of ROS such as $O_2^{\cdot-}$ and $^{\cdot}OH$ with temperature of soil heating. Since ROS are considered toxic for life (Zhao et al.

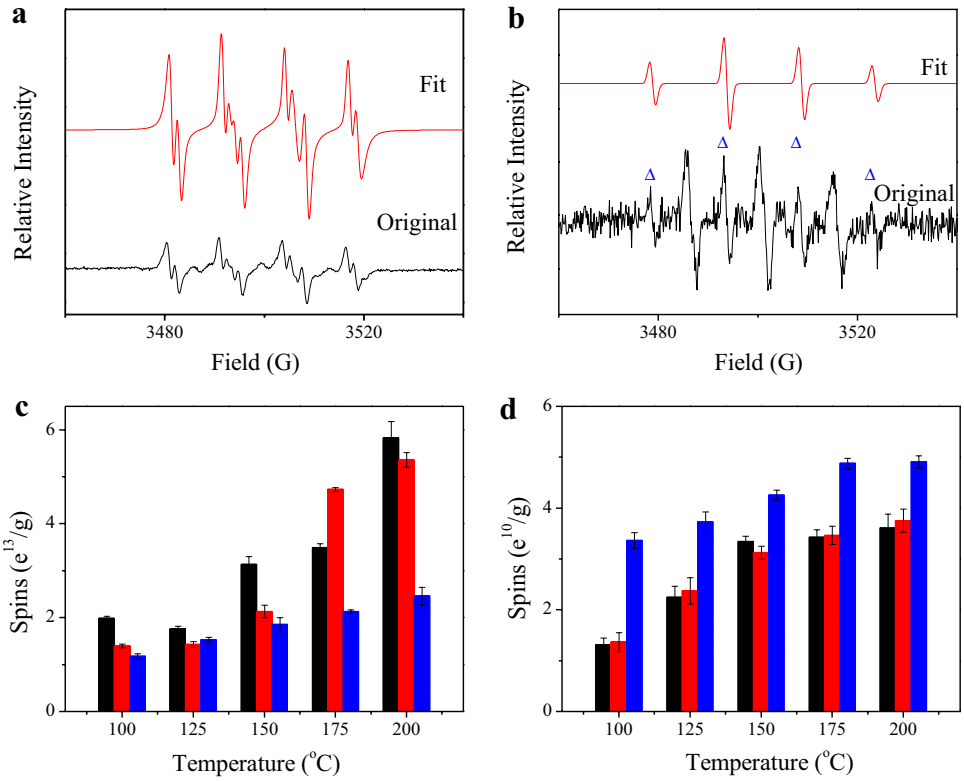

Fig. 3 Formation of reactive oxygen species (ROS) in benzo[a]pyrene-spiked bauxite soil, after heating 1 h at 100–200 °C. **a** Identification of $O_2^{\cdot-}$; 'original' means the signal of $O_2^{\cdot-}$ in benzo[a]pyrene-spiked bauxite soil after 1 h of thermal treatment at 175 °C; 'fit' represents the fitting of $O_2^{\cdot-}$. **b** Identification of $^{\cdot}OH$; 'original' means the signal of $^{\cdot}OH$ in benzo[a]pyrene-spiked bauxite soil after 1 h of thermal treatment at 175 °C; 'fit' represents the fitting of $^{\cdot}OH$. **c** Concentration of $O_2^{\cdot-}$ versus temperature. **d** Concentration of $^{\cdot}OH$ versus temperature. Note the increase in ROS versus temperature (°C)

2019), this finding implied that thermal treatment of soils might not be a perfect technique to remediate PAHs-polluted soils.

Conclusion

We studied the formation of EPFRs in benzo[a]pyrene contaminated soils heated at 100–200 °C during 1 h. Results showed that the concentration of EPFRs increased up to maximum at 175 °C and then decreased. Moreover, the 1/e lifetimes of EPFRs formed by heat treatment were very long, reaching to at least 757.58 h. The thermally treated soil readily induced the generation of ROS, including $O_2^{\cdot-}$ and $^{\cdot}OH$, which correlated with the formation of benzo[a]pyrene–EPFRs in soil. Our findings imply that soil treatment at low temperature may not be so sustainable and clean as previously assumed because EPFRs may induce toxicity for living organisms.

Acknowledgements Financial supports by the National Natural Science Foundation of China (Grants Nos. 41571446 & 41877126), the "Open Project" of the State Key Laboratory of Pollution Control and Resource Reuse (PCRRF17020) and the "One Hundred Talents" program of Shaanxi Province (SXBR9171) are gratefully acknowledged.

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Supplementary Material

Formation of environmentally persistent free radicals and reactive oxygen species during the thermal treatment of soils contaminated by polycyclic aromatic hydrocarbons

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Text S1 Soil texture was determined by the hydrometer method (Wen et al. 2002). The content of OC was measured using a total organic carbon (TOC) analyzer from Elementar vario series, Hesse-Darmstadt. For metal contents, soil samples were completely digested by microwave using the Aqua Regia solution of 3/1 37%HCl / 97%HNO_3 (Janssen et al. 1997). Concentration of metal ions in digestion solutions was measured by an inductively coupled plasma atomic emission spectrometer (ICP-AES) from Thermo-ICAP6300, Waltham. For pH determination, a 1/5 w/v mixture of soil in Milli-Q water with soil and solution was placed into a shaker for 1h, then settled before measuring pH. Cation exchange capacity (CEC) was obtained by adding 0.2 M NH_4Cl to substitute exchangeable cations, such as K^+, Na^+, Ca^{2+}, Mg^{2+}, Al^{3+}, into supernatant from the three consecutive washes, then were analyzed by ICP-AES. The clay granulometric fraction, referring to less than 2 mm particles, was analyzed semi-quantitatively by X-ray diffraction analysis (XRD, D8-ADVANCE) to identify the constitution of clay minerals in soils.

Text S2 Specifically, 50 mg soil was extracted by 1 mL acetone and dichloromethane 1/1 v/v under sonication for 15min. The suspension was then centrifuged for 5 min at 20,000 g to separate the solid from solvents. To ensure the complete extraction of organic compounds from soil samples, the extracting procedure was conducted for three times. Supernatants were collected and filtered using a syringe equipped with a 0.45 μm membrane filter. Finally, the filtrate was placed in amber vial and analyzed for the concentration of benzo[a]pyrene using a HPLC equipped with a 25 cm × 4.6 mm, 5 μm Cosmosil C18 column. A sample volume of 10 μL was injected into the HPLC by an autosampler. The total run time was 10 min. HPLC conditions were: 100% methanol as mobile phase; flow rate of 1 mL min^{-1}; oven temperature 30 °C; UV wavelength of benzo[a]pyrene at 384 nm.

Text S3 EPR instrument operating parameters were center field 3500 G; microwave frequency 9.8 GHz; microwave power 2.0 mW; modulation frequency 4.0 G; modulation amplitude 4.0 G; sweep width 200 G; receiver gain 3.54 × 104; time constant 41.0 ms; sweep time 15 s; 15 scans. Radical concentrations were calculated by comparing the signal peak area, as derived from $(\Delta H_{p-p})^2$ multiplied by the relative intensity, to a 2,2-diphenyl-1-picrylhydrazyl standard. Radical quantification was evaluated using Bruker's Xenon program according to the quantitative theory of spin calculation. Solution spectra were simulated with the Spin Fit (Bruker's Xenon program); the software provided an automatic fit to the experimental spectrum and determined the relative intensity of each spin adducts.

Text S4 After soil storage during 12-168 h in the dark, samples were extracted and subjected to EPR analysis. EPR spectra were calculated to obtain the spins density of radicals as a function of time. Subsequent analyses were normalized to initial concentration of EPFRs. In order to calculate the decay rate constants and 1/e lifetimes of EPFRs, the plotted date was subjected to exponential regression. The 1/e lifetimes of EPFRs were evaluated using the following mathematical expression for the first-order decay:

$\mathrm{Ln}\ (R/R_0) = -kt$, and $t_{1/e} = 1/k$

Where R_0 was the initial highest concentration of EPFRs, and R was the concentration of the detected EPR signal periodically. Rate constant k was obtained from the slope of the correlation between logarithm of radical concentration change (R/R_0) versus time, and 1/e lifetimes were calculated accordingly.

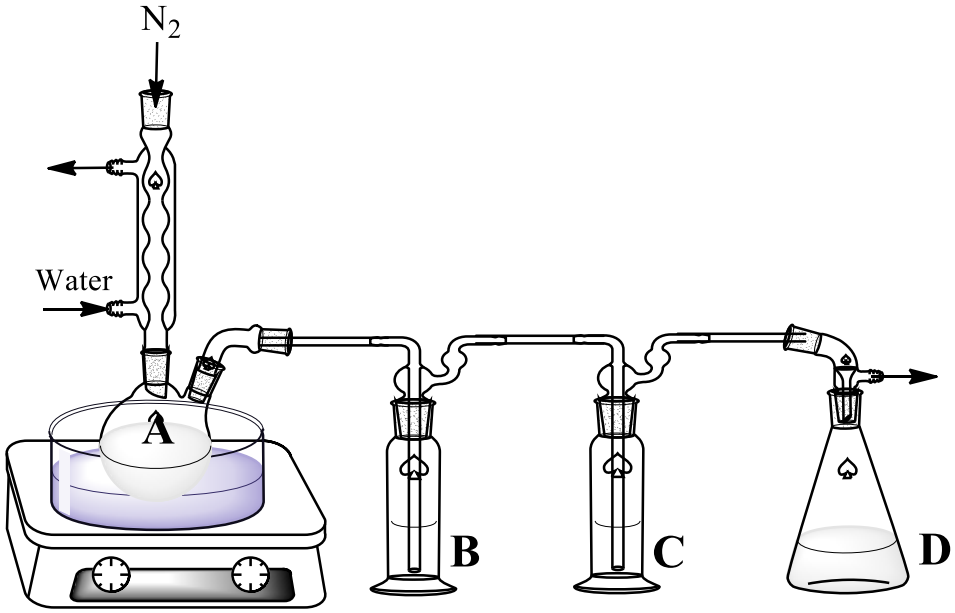
Table S1. Physicochemical properties of sampled soils and quartz particles.

Soil characteristic	Soil sample			
	A	B	C	D
Location	Shannxi 34°11′ N 113°01′ E	Henan 35°00′ N 113°41′ E	Heilongjiang 45°40′ N 126°37′ E	
Soil type	Bauxite soil	Fluvo-aquic soil	Chernozem soil	Quartz particles
pH	7.90	8.07	6.27	7
OC*, wt %	0.956	1.032	2.07	n.d.
Clay, wt %	26.01	18.18	19.33	n.d.
CEC**, cmol/kg	22.37	16.01	28.59	n.d.
Total Fe, g/kg	17.13	20.76	25.56	n.d.
Total Mn, g/kg	0.37	0.46	0.63	n.d.
Total Cu, g/kg	/	/	/	n.d.
Total Zn, g/kg	0.06	0.07	0.13	n.d.
Total Pb, g/kg	/	/	0.09	n.d.
Total Mg, g/kg	5.72	7.98	5.20	n.d.
Total Ca, g/kg	90.89	141.28	23.24	n.d.

n.d.: not detected

*OC: organic carbon.

**CEC: cation exchange capacity.



Scheme S1. Pictorial diagram of the experimental device. A, two-necked round bottom flask; B and C, porous gas washing bottles; D, round-bottomed flask filled with water. The samples in A was collected and extracted after thermal treatment, then the residual benzo[a]pyrene, the environmentally persistent free radicals (EPFRs) and reactive oxygen species (ROS) were measured.

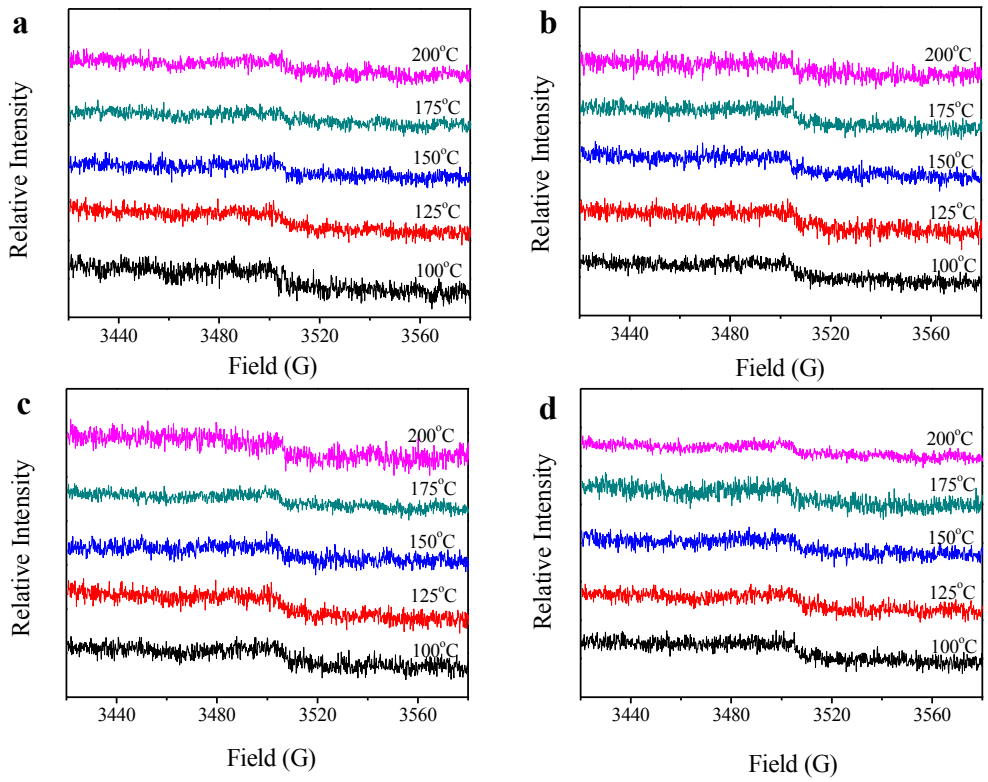


Figure S1 Environmentally persistent free radicals (EPFRs) signals after thermal treatment in non-polluted quartz particles and uncontaminated soils: quartz particles (a), bauxite (b), fluvo-aquic soil (c) and chernozem (d). Note the small signal in quartz particles and three soils, meaning that benzo[a]pyrene is needed to produce radicals.

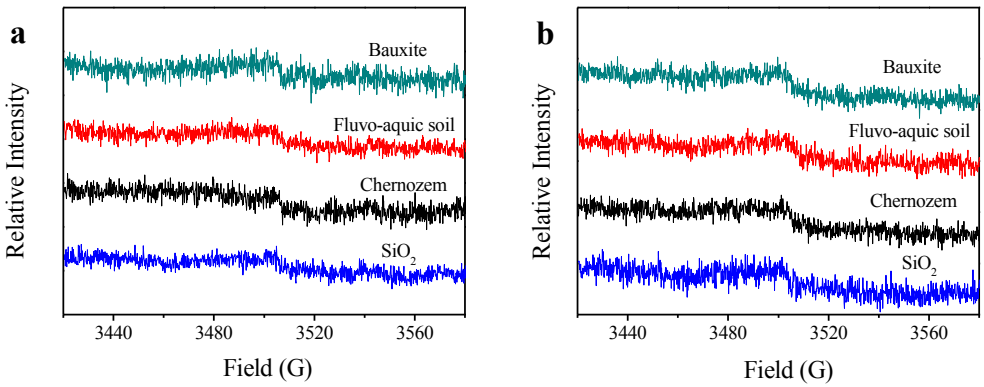


Figure S2 Environmentally persistent free radicals (EPFR) signals before thermal treatment in noncontaminated soils, quartz particles (a) and benzo[a]pyrene contaminanted soils, quartz particles (b). Note the small signals in quartz particles and three soils, meaning that thermal treatment is needed to produce radicals.

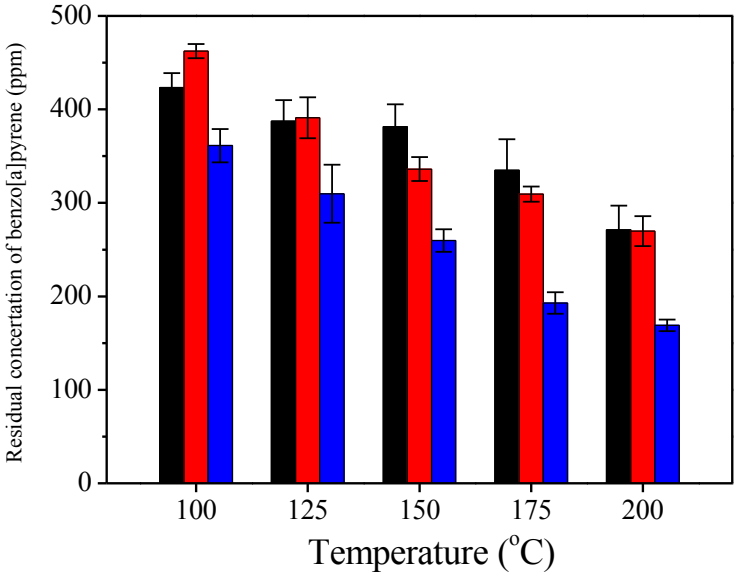


Figure S3 Residual concentration of benzo[a]pyrene in three soils after thermal treatment at 100-200°C. Note the residual concentration of benzo[a]pyrene in all three soils decreased with increasing temperature.

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