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High contribution of hydrocarbon transformation during the removal of polycyclic aromatic hydrocarbons from soils, humin and clay by thermal treatment at 100–200 °C

Hanzhong Jia[1] · Jinbo Liu[1] · Kecheng Zhu[1] · Pin Gao[2] · Eric Lichtfouse[3]

Abstract
Polycyclic aromatic hydrocarbons (PAHs) are major pollutants in air, soils and sediments. PAH-polluted soils can be cleaned rapidly by thermal treatment. PAH volatilization is considered as the main process explaining PAH removal at low temperature, yet other processes may occur. Particularly, we hypothesize that thermal transformation can also explain PAH removal, where transformation refers to both degradation and formation of bound PAHs. We thus studied the removal of spiked benzo[a]pyrene at 0.5 mg/g in bauxite soil, fluvo-aquic soil, chernozem soil, montmorillonite, humin, and quartz sand as control, from 100 to 200 °C. We measured concentrations of benzo[a]pyrene in the volatilized fraction and solid residues by high-performance liquid chromatography. We identified transformation products by gas chromatography–mass spectrometry. Results show that the contribution of thermal transformation to the removal of benzo[a]pyrene increased from 24.7 to 58.4 wt% for bauxite soil, from 4.4 to 38.2 wt% for fluvo-aquic soil, and from 11.5 to 35.9 wt% for chernozem soil, with temperature increasing from 100 to 200 °C. Transformation such as oxidation occurred in all samples except in benzo[a]pyrene-spiked quartz sands. Transformation of benzo[a]pyrene was thus partly explained by the presence of clay minerals, as evidenced for the montmorillonite assay where transformation contributed 74.6 wt% to the total removal of benzo[a]pyrene at 200 °C. Overall, our findings demonstrate a major overlooked contribution of transformation to PAH removal at low temperature.

Keywords Thermal treatment · Polycyclic aromatic hydrocarbon · Benzo[a]pyrene · Transformation · Volatilization · Clay minerals

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of priority organic pollutants according to the US Environmental Protection Agency. PAHs induce teratogenic, carcinogenic and mutagenic effects in living organisms (Juhasz and Naidu 2000; Li et al. 2008; Samanta et al. 2002). About 90% of environmental PAHs ultimately end up into soils and sediments, notably due to their excellent hydrophobic property (Eriksson et al. 2000; Field et al. 1992). After entering soils and sediments, PAHs are hardly degraded due to their chemical stability, oxidation resistance and environmental persistence (Jafarabadi et al. 2018; Lichtfouse et al. 1997; Zhang et al. 2015). Therefore, rapid and effective methods are needed to remove PAHs from contaminated soils (Henner et al. 1997).

Remediation techniques for PAH-contaminated soils include chemical oxidation (Si-Hyun et al. 2009), washing

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(Trellu et al. 2016), thermal treatment (Bucala et al. 1994; Li et al. 2018) and bioremediation (Gan et al. 2009; Harvey et al. 2002; Wilson and Jones 1993). Thermal treatment is used for fast and efficient remediation (Merino and Bucalá 2007). Two types of thermal treatment are distinguished according to the process involved: desorption at low temperatures of 100–300 °C and degradation at high temperatures of 300–600 °C (Falciglia et al. 2011). High-temperature treatments remove more organic compounds, but require more energy and strongly alter soil physicochemical properties. Alternatively, low-temperature treatment causes minimal damage to soils, requires lower energy, yet still removes organic pollutants efficiently (Falciglia et al. 2011). As a consequence, low-temperature treatment is widely applied to remediate contaminated soils (Gilot et al. 1997; Falciglia et al. 2011; Merino and Bucalá 2007).

The main mechanisms proposed to explain removal of organic pollutants from soils by low-temperature treatment are volatilization and desorption (Falciglia et al. 2011; Gilot et al. 1997; Merino and Bucalá 2007; Talley et al. 2004). Nevertheless, recent investigations suggest that catalyzed oxidation might occur during low-temperature treatment of contaminated soils (Wang et al. 2015; Zhang et al. 2019). For example, Zhang et al. (2019) found that oxidation was a major process during thermal treatment of catechol-contaminated soils. Jia et al. (2019) further reported that minerals can induce oxidation of PAHs even under natural conditions. These observations suggest that oxidative transformation might contribute to PAH removal at low temperature. However, there is actually little quantitative knowledge on the contribution of PAH transformation versus volatilization during thermal treatment of PAH-contaminated soils at low temperature. Therefore, we investigated the transformation and volatilization of benzo[a]pyrene, a carcinogenic PAH, from benzo[a]pyrene-spiked soils to explore the underlying removal mechanisms.

Materials and methods

Chemicals

Benzo[a]pyrene, of 98% purity, HPLC-grade methanol, was purchased from J&K Chemical Ltd., Beijing, China. Dichloromethane and acetone of analytical grade were from Sinopharm Chemical Reagent Co., Shanghai, China. 100 mesh acid-purified quartz sands were from Tianjin Kemiou Chemical Reagent Co., Tianjin, China. SWy-3 montmorillonite was from the Clay Minerals Society, West Lafayette, USA. Humin was extracted from peat according to the method of the International Humic Substances Society (IHSS) (Saab and Martin-Neto 2008).

Soil sample collection and benzo[a]pyrene-spiked sample preparation

Three cultivated soils including bauxite soil, fluvo-aquic soil and chernozem soil were sampled from the 0–20 cm soil surface layer in Shaanxi, Henan and Heilongjiang provinces in China, respectively. Soils were air-dried for 24 h at 25 °C and sieved through 100-mesh prior to analysis.

Benzo[a]pyrene-spiked soil samples were prepared with previously described methods (Jia et al. 2018; Zhao et al. 2017). Samples included three soils: bauxite soil, fluvo-aquic soil and chernozem soil, and pure components: montmorillonite, humic acid and quartz sands. Typically, 1 g of sample was mixed with 1 mL of acetone containing 500 mg/L of benzo[a]pyrene. The sample-benzo[a]pyrene suspensions were mixed for 0.5 h and then placed in the dark at 25 °C until acetone was completely evaporated in about 5 min. The final concentration of benzo[a]pyrene in samples was determined after extracting by a mixture of acetone and dichloromethane (1/1 v/v), and the concentration values were in the range of 0.497–0.502 mg/g. The prepared samples were stored at −4 °C before use.

Low-temperature treatment

Samples contaminated with benzo[a]pyrene were heated using an experimental apparatus (Fig. 1), consisting of an oil bath heater from DragonLAB, MS-H-Pro$^+$, China, a two-necked round-bottom flask, two porous gas washing bottles for capturing volatilized-benzo[a]pyrene by a mixture of acetone and dichloromethane (1/1 v/v), and a round-bottomed flask filled with water to absorb the exhaust gas. As the oil bath temperature reached 100, 125, 150, 175 or 200 °C, the two-necked round-bottom flask was put into the oil bath and kept for 60 min. After that, soil samples were collected and cooled down at 25 °C and then stored in the sealed polyethylene bags prior to analysis. The solution in porous gas washing bottles was collected and dried to 5 mL by a rotary evaporator from DragonLAB, RE100-Pro, China, and then analyzed using a U3000 high-performance liquid chromatograph (HPLC) from Thermo Scientific, Germering, Germany. Blanks of non-spiked samples and control of benzo[a]pyrene-spiked quartz sands were thermally treated in parallel as mentioned above. Each treatment was repeated three times. The removal (%*Re*) including transformed- and volatilized-benzo[a]pyrene are calculated as follows

$$\%\mathrm{Re} = \frac{M_0 - M_\mathrm{f}}{M_0} \times 100 = \%\mathrm{Re}_{\mathrm{transformed}} + \%\mathrm{Re}_{\mathrm{volatilized}}$$

where %Re corresponds to the total removal of benzo[a]pyrene after thermal treatment, M_0 and M_f correspond,

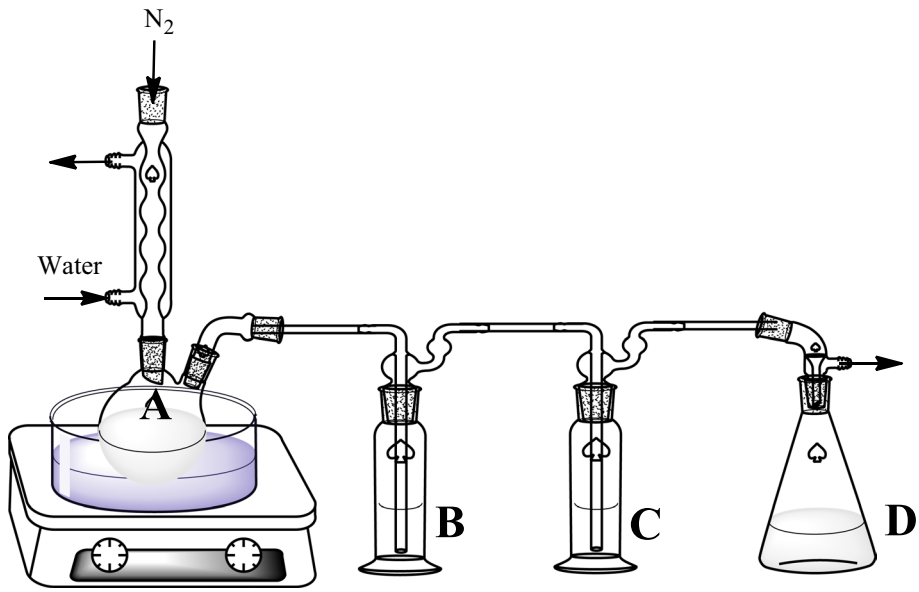

Fig. 1 Experimental apparatus for the thermal treatment of benzo[a]pyrene-spiked sand, montmorillonite, humin and soils. **A**, two-necked round-bottom flask; **B** and **C**, porous gas washing bottles; **D**, round-bottomed flask filled with water. The samples in **A** was collected and extracted after thermal treatment, and then, the residual benzo[a]pyrene was measured. The volatilized-benzo[a]pyrene was adsorbed by solvents in both **B** and **C** and then mixed for measurement

respectively, to the initial and final extractable amounts of benzo[a]pyrene in the samples, $\%Re_{transformed}$ and $\%Re_{volatilized}$ correspond, respectively, to the removal of benzo[a]pyrene by transformation and volatilization.

Chemical analysis

Organic carbon (OC), clay and metal contents, pH and cation exchange capacity (CEC) of the collected soil samples were determined with methods previously reported by Droge and Goss (2013). Briefly, the soil OC was measured by a total organic carbon (TOC) analyzer from Elementar vario series, Hesse-Darmstadt, Germany. To analyze metals, soil samples first were fully microwave-digested in aqua regia solutions (Janssen et al. 1997). The resulting digested solutions were measured using inductively coupled plasma atomic emission spectrometer (ICP–AES) from Thermo Scientific iCAP6300, Waltham, USA. For measuring pH, 5 g of soil was mixed with 25 mL of deionized water (1/5 m/v soil to water ratio) for 1 h, and then, the supernatant pH was measured. Cation exchange capacity (CEC) was determined by adding 0.2 M NH_4Cl into the supernatant for substituting exchangeable cations of K^+, Na^+, Ca^{2+}, Mg^{2+}, and Al^{3+} and then analyzed by ICP–AES. Clays in particle-size fractions below 2 mm of the target soils were determined semi-quantitatively by X-ray diffraction analysis (XRD, D8-ADVANCE). Soil textures were analyzed using a hydrometer method (Wen et al. 2002).

After thermal treatment, 50 mg of each sample was sacrificed and extracted by 1 mL of a mixture of acetone and dichloromethane (1/1 v/v) for three cycles. Extracts were collected and mixed and then filtrated using syringes with 0.45 μm membrane filters. Benzo[a]pyrene in the filtrate was quantified by HPLC equipped with a Cosmosil C18 column (25 cm × 4.6 mm, 5 μm particle size). Pure methanol was used as mobile phase in isocratic mode with a flow rate of 1.0 mL/min. The sample injection volume was 10 μL with an auto-sampler. The oven temperature was kept at 30 °C.

Thermal transformation products were identified with an Agilent 7890B–5977B gas chromatograph–mass spectrometer (GC–MS) by scanning from m/z 40 to m/z 500. A Rtx-5MS capillary column of 30 m × 0.25 mm internal diameter (i.d.) and 0.25 μm film thickness was used, and the He flow rate was 1.0 mL/min. The temperature program for separation started at 80 °C and held for 2 min, set at 10 °C/min to 290 °C and held for 10 min. The inlet temperature was 290 °C, and the detector temperature was 200 °C.

Results and discussion

Amount of removal of benzo[a]pyrene

We studied the transformation and volatilization of benzo[a]pyrene in the benzo[a]pyrene-spiked samples after 60 min at 100–200 °C. Samples included three soils: bauxite soil, fluvo-aquic soil and chernozem soil, and pure components: montmorillonite, humin, and quartz sands. Uncontaminated samples were also run under the same conditions as blanks.

Our results show that the removal of benzo[a]pyrene (*%Re*) in all samples increased with temperature (Fig. 2). For example, the concentration of benzo[a]pyrene in the bauxite soil decreased from 0.501 to 0.362 mg/g at 100 °C for 60 min. At 200 °C, the concentration of benzo[a]pyrene reduced to 0.169 mg/g, resulting in a removal 0.193 mg of benzo[a]pyrene. Similar results were also obtained for fluvo-aquic and chernozem soils, with reduction of

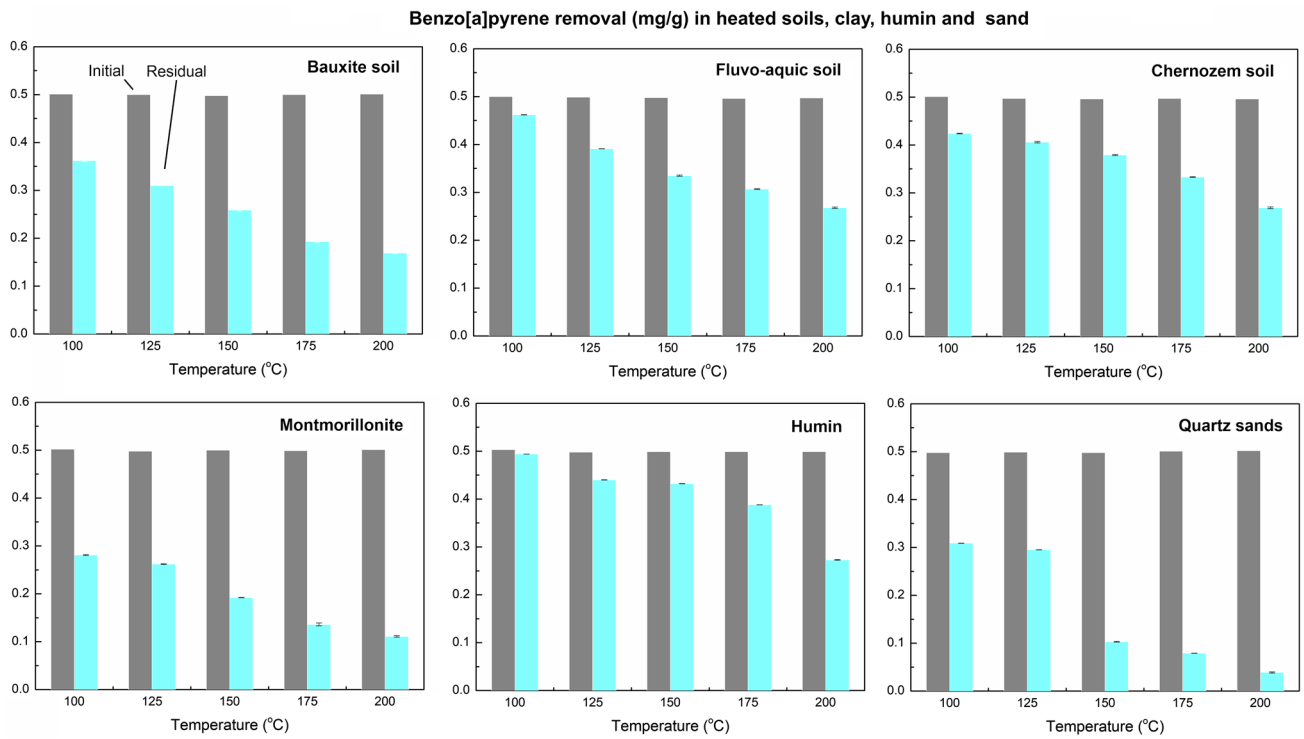

Fig. 2 Removal of benzo[a]pyrene in bauxite soil, fluvo-aquic soil, chernozem soil, montmorillonite, humin, and quartz sands during thermal treatment from 100 to 200 °C. Gray bars show the initial concentration of spiked benzo[a]pyrene. Blue bars depict the residual concentration of benzo[a]pyrene after treatment. Note the increasing removal with temperature, the highest removal for pure quartz sands, the high removal for montmorillonite clay and the low removal for humin, a major soil organic component. Those findings reveal the strong interactions of soil components with PAHs, either promoting removal for clays, or inhibiting removal for humin

benzo[a]pyrene of 0.194 mg and 0.155 mg, respectively. These results are consistent with previous reports (Falciglia et al. 2011; Talley et al. 2004).

We observed the highest removal of benzo[a]pyrene in pure quartz sands, reaching 92.2% at 200 °C (Fig. 2). This finding suggests that soil components such as organic matter and minerals display strong interactions with PAHs during thermal treatment. These interactions either promote or inhibit PAH removal. For instance, montmorillonite promotes benzo[a]pyrene removal, with a high decrease of concentration to 0.111 mg/g at 200 °C, in agreement with our previous report on the impact of clays (Jia et al. 2016). On the contrary, results show that humin, a major organic component, inhibits benzo[a]pyrene removal, with a concentration almost unchanged (0.494 mg/g) versus initial concentration (0.503 mg/g), at 100 °C for 60 min. This protecting effect is also observed in fluvo-aquic and chernozem soils.

Overall, our results demonstrate the strong interactions of benzo[a]pyrene with soil components, either promoting removal by clays or inhibiting removal by organic matter. The next section deciphers removal mechanisms, in particular the respective contribution of PAH transformation versus PAH volatilization.

Mechanisms of removal of benzo[a]pyrene

Volatilization

Here, we assume that the removal of benzo[a]pyrene during thermal treatment is explained either by PAH volatilization or PAH transformation, in which transformed-benzo[a]pyrene includes thermal-degraded, e.g., oxidized, and soil-bound benzo[a]pyrene. Results show that proportion of volatilized-benzo[a]pyrene in all samples increased with temperature from 100 to 200 °C (Fig. 3, orange bars). For instance, using cultivated soils, the volatilized-benzo[a]pyrene accounted, respectively, for 3.1–7.8 wt% in the bauxite soil, 3.1–7.9 wt% in the fluvo-aquic soils, and 3.9–9.9 wt% in the chernozem soil. Similarly, volatilization accounted ti 1.4–3.2 wt% for montmorillonite and 0.6–1.4 wt% for humin, in agreement with a previous report (Karimi-Lotfabad et al. 1996). By contrast, using pure quartz sands, volatilization accounted up to 97.3 wt% of removal. These findings reveal that the interaction of soil components with benzo[a]pyrene strongly reduce volatilization.

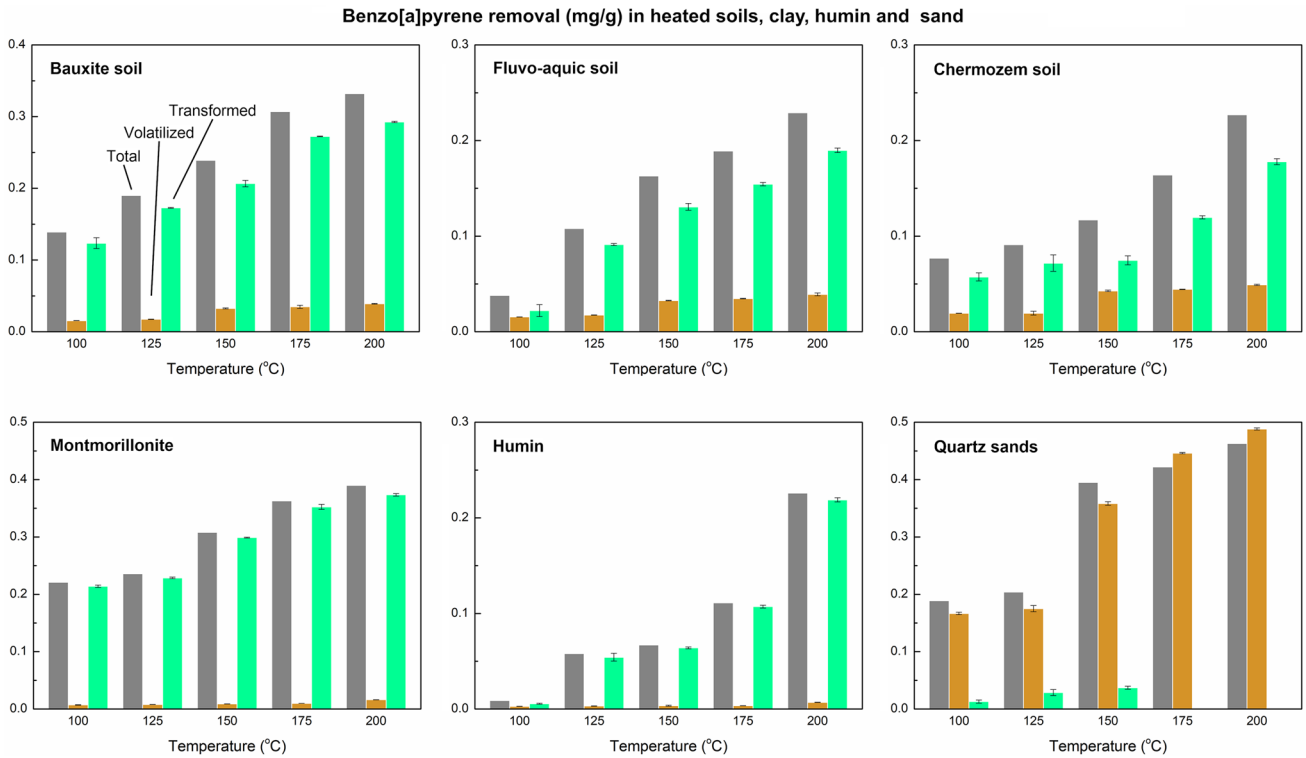

Fig. 3 Contribution of volatilized-benzo[a]pyrene (orange) and transformed-benzo[a]pyrene (green) to its total removal amount (grey) in bauxite soil, fluvo-aquic soil, chernozem soil, montmorillonite, humin and quartz sands during thermal treatment from 100 to 200 °C. Note the high contribution of transformation versus volatilization, except in quartz sand. This finding reveals the major contribution of soil components, in particular clay and organic matter, to the transformation of benzo[a]pyrene. Transformation refers both to degraded, e.g., oxidized benzo[a]pyrene, and benzo[a]pyrene sequestrated into soil organic matter

Transformation

The concentration of transformed-benzo[a]pyrene increased with temperature and, more importantly, accounted for a much higher proportion of removal (Fig. 3, green bars) compared to volatilization. For example, transformation accounted for 24.7–58.4 wt% in the bauxite soil, 4.4–38.2 wt% in the fluvo-aquic soil, and 11.5–35.9 wt% in the chernozem soil. By contrast, transformation was very low in pure quartz sands. These findings reveal again the strong interactions of benzo[a]pyrene with two soil components, clays and organic matter. Indeed, results for the montmorillonite clay display a 42.7–74.6 wt% contribution of transformation. The clay influence is also supported by the clay content of our soil samples, of 26 wt% for the bauxite soil, 18.2 wt% for the fluvo-aquic soil and 19.3 wt% for the chernozem soil. These observations are supported by our previous studies showing that benzo[a]pyrene interacts with the clay surface via cation-π complexation, then promotes electron transfer followed by oxidation (Jia and Wang 2013; Jia et al. 2016). Alternatively, transformation of benzo[a]pyrene may be triggered by oxidative degradation in the presence of manganese and iron oxide in soil during heating (Umeh et al. 2018), as suggested by the presence of Mn and Fe in our soil samples (Table S1). Overall, minerals such as clays are likely to play a major role in benzo[a]pyrene transformation.

Concerning the role of organic matter, results for humin show up to 43.9 wt% of transformed-benzo[a]pyrene at 200 °C (Fig. 3). This observation is supported by the formation of humin-bound hydrophobic compounds such *n*-alkanes (Lichtfouse et al. 1998a, b) and benzo[a]pyrene (Zeng et al. 2018). PAHs strongly adsorb onto organic matters (Celis et al. 2006), thus enhancing PAH retention in soils and inhibiting the mineral-mediated transformation (Jia et al. 2015).

Overall, our findings show that transformation accounts for a major proportion of benzo[a]pyrene removal in soils, clay and humin, versus volatilization, during thermal treatment at 100-200 °C. Transformation of benzo[a]pyrene is explained by two possible processes, sequestration into soil organic matter as humin-bound compounds and oxidative degradation, the quantitative contribution of which is unknown. We further gained insights on the oxidation process by studying degradation products in the next section.

Mechanisms of thermal degradation of benzo[a] pyrene

Further insights on the contribution of thermal degradation to the transformation of benzo[a]pyrene was obtained by gas chromatography–mass spectrometry (GC–MS). For quartz sands as control assay, benzo[a]pyrene is a major compound (Fig. 4a). This finding is consistent with our results showing that almost all of the spiked benzo[a]pyrene, about 97.3 wt%, in quartz sands was volatilized during thermal treatment at

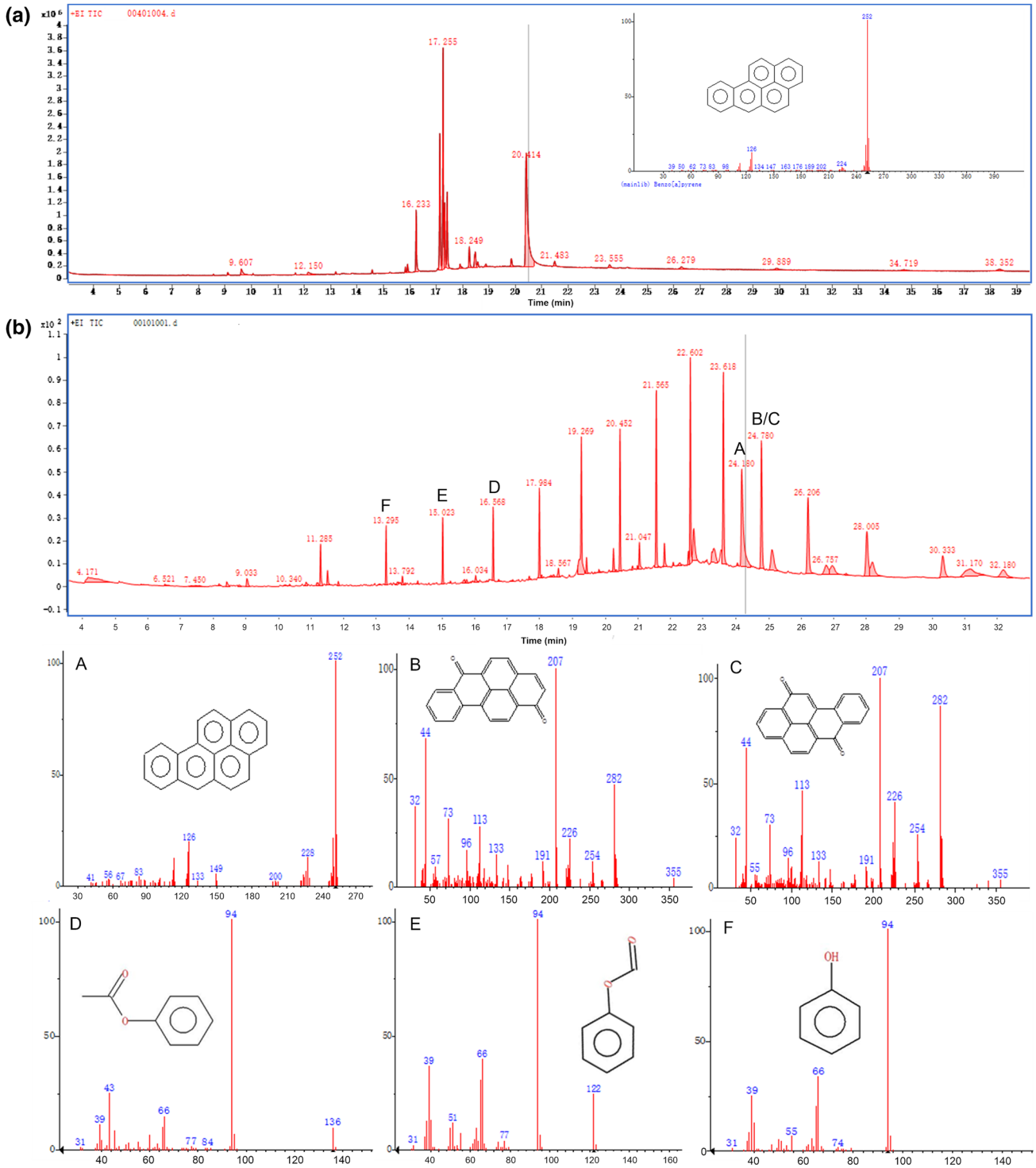

Fig. 4 Total ion current and mass spectra of products of thermal treatment of benzo[a]pyrene-spiked samples, for quartz sand (**a**) and the bauxite soil (**b**), obtained by gas chromatography–mass spectrometry (GC–MS)

200 °C (see previous section). In contrast, several degradation products were identified in benzo[a]pyrene-spiked soils, i.e., in the bauxite soil, such as benzo[a]pyrene-1,6-dione, benzo[a]pyrene-6,12-dione, formic acid phenyl ester, acetic acid phenyl ester, and phenol (Fig. 4b). Noteworthy, some of those compounds were also observed in the Fenton oxidation of benzo[a]pyrene (Lee and Hosomi 2001). Our findings thus confirm the occurrence of oxidative transformation of benzo[a]pyrene during thermal treatment at 100–200 °C.

Thermal degradation may be induced by electron transfer between benzo[a]pyrene molecules and clay minerals (Jia et al. 2016). This assumption is strengthened by findings showing that benzo[a]pyrene can be adsorbed on clays by complexation of exchangeable cations on mineral surfaces (Celis et al. 2006). Direct electron transfer from benzo[a]pyrene molecules to the active sites of soil minerals may thus occur, producing the electron-deficient intermediates. In turn, these unstable intermediates react with dioxygen to form oxygenated compounds (Zhao et al. 2017). Oxidation is also supported by the reported production of reactive oxygen species (ROS) during thermal treatment (Zhang et al. 2019). ROS may thus react with adsorbed benzo[a]pyrene to generate oxidative cleavage products. As a result, oxidation is likely to contribute to the removal of benzo[a]pyrene by thermal treatment.

Conclusion

We studied the mechanisms for benzo[a]pyrene removal in soils during thermal treatment at 100–200 °C. Results showed that heating temperature and soil components had significant impacts on the volatilization and transformation of benzo[a]pyrene. The contribution of thermal transformation to the removal of benzo[a]pyrene increased with temperature. Clay minerals such as montmorillonite promote the oxidation of benzo[a]pyrene, producing oxygenated-benzo[a]pyrene and other aromatic compounds. Transformation, rather than volatilization, accounts for a major part of benzo[a]pyrene removal in soils at 100–200 °C.

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SUPPLEMENTARY MATERIAL

High contribution of hydrocarbon transformation during the removal of polycyclic aromatic hydrocarbons from soils, humin and clay by thermal treatment at 100-200 °C

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Table S1

Physicochemical properties of bauxite soil, fluvo-aquic soil, chernozem soil, montmorillonite, and humin.

Soil characteristics	Sample				
	Bauxite	Fluvo-aquic soil	Chernozem	Montmorillonite	Humin
Location	Shannxi 34°11′N, 113°01′E	Henan 35°00′N, 113°41′E	Heilongjiang 45°40′N, 126°37′E		
pH	7.90	8.07	6.27	6.54	7.00
OC*, wt%	0.96	1.03	2.07		7.89
Clay, wt%	26.01	18.18	19.33	100.00	
CEC**, cmol/kg	22.37	16.01	28.59		
Total Fe, g/kg	17.13	20.76	25.56	12.80	3.60
Total Mn, g/kg	0.37	0.46	0.63	0.09	0.07
Total Cu, g/kg	/	/	/	/	/
Total Zn, g/kg	0.06	0.07	0.13	0.09	0.03
Total Pb, g/kg	/	/	0.09	/	0.02
Total Mg, g/kg	5.72	7.98	5.20	7.40	0.30
Total Ca, g/kg	90.9	141.3	23.2	24.5	7.1

* OC: organic carbon.

**CEC: cation exchange capacity.