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Review

Formation mechanisms and degradation methods of polycyclic aromatic hydrocarbons in biochar: A review

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ABSTRACT

Biochar has been widely used in soil amendment and environmental remediation. Polycyclic aromatic hydrocarbons (PAHs) could be produced in preparation of biochar, which may pose potential risks to the environment and human health. At present, most studies focus on the ecotoxicity potential of biochar, while there are few systematic reviews on the formation mechanisms and mitigation strategies of PAHs in biochar. Therefore, a systematical understanding of the distribution, formation mechanisms, risk assessment, and degradation approaches of PAHs in biochar is highly needed. In this paper, the distribution and content of the total and bioavailable PAHs in biochar are reviewed. Then the formation mechanisms, influencing factors, and potential risk assessment of PAHs in biochar are systematically explored. After that, the effective strategies to alleviate PAHs in biochar are summarized. Finally, suggestions and perspectives for future studies are proposed. This review provides a guide for reducing the formation of biochar-associated PAHs and their toxicity, which is beneficial for the development and large-scale safe use of environmentally friendly biochar.

1. Introduction

Biochar is a highly aromatic porous carbonaceous material produced by pyrolysis under anoxic or limited oxygen conditions (Lehmann, 2007; Lehmann et al., 2006). Biochar has been widely utilized as an adsorbent, soil amendment, and catalyst due to its multifunctional properties and low-production cost (Qin et al., 2020; Wang et al., 2019a, 2020b; Zhang et al., 2022b; Zhao et al., 2022a). For example, different organic and inorganic pollutants (Feng et al., 2022; Wang et al., 2020a), including heavy metals (Zhao et al., 2021), dyes, and agrochemicals (Masrura et al., 2022) can be adsorbed by biochar from solid and liquid phases (Qin et al., 2020; Wang et al., 2018a). Biochar can reduce the mobility and bioavailability of pollutants and suppress their potential toxicity (Sakhiya et al., 2020; Tan et al., 2015; Wang et al., 2022). In addition, as a soil amendment, biochar can improve the pH of acidic soils, ion exchange capacity, microbial activity, carbon storage, and crop yield (Abukari et al., 2022; Gao et al., 2022; Yuan et al., 2019; Zhao et al., 2022b). Nevertheless, biochar may contain potentially toxic substances, such as polycyclic aromatic hydrocarbons (PAHs), dioxin, heavy metals (Huang et al., 2022; Meng et al., 2022), metal hydrides (Luo et al., 2020), and persistent free radicals (Odinga et al., 2020) depending on different feedstocks and pyrolysis conditions. Among them, PAHs could be produced during the preparation of biochar (Wang et al., 2017; Yang et al., 2019), and PAHs content was relatively higher than associated substances (such as Dioxin 0–610 pg/g) (Godlewska et al., 2020). PAHs are toxic, mutagenic, and cancerogenic compounds classified as organic pollutants. The application of PAHs-containing biochar to agricultural soil may lead to potential risks to the environment. For example, the application of biochar to soil increased the concentration of PAHs in crops (Wang et al., 2019b). Some plant root exudates promote the release of PAHs in biochar, which may increase environmental pollution (Wang et al., 2019b, 2020c). Therefore, understanding the distribution and formation of PAHs is of great significance for pollution control and safe utilization of biochar.

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In recent years, the formation, occurrence distribution, and analysis of PAHs in biochar has been reported (Krzyszczak et al., 2021; Wang et al., 2017; Zhang et al., 2020). The concentration of PAHs in some biochar was higher than the environmental quality standards (International Biochar Initiative (IBI) standard), depending on feedstocks and pyrolysis conditions (IBI, 2015; Wang et al., 2019b). Pyrolysis type, pyrolysis temperature, feedstock, heating rate, type of carrier gas, and reaction time can affect the type and quantity of PAHs produced during the pyrolysis of biomass. Compared with slow pyrolysis, fast pyrolysis produces more PAHs, such as fluorene, anthracene, phenanthrene, and pyrene (Safdari et al., 2019). The concentration of PAHs initially increased and then decreased as the pyrolysis temperature increased (Gao et al., 2016). Research shows that pyrolysis temperature is the most important factor affecting the formation of PAHs, as it can not only increase the number of PAHs, but also change the molecular weight of PAHs. PAHs with low molecular weight (LMW) are usually formed at low temperatures (<500 °C), while PAHs with high molecular weight (HMW) are usually formed at high temperatures (>500 °C) (Wang et al., 2017). Previous reviews on the formation mechanisms of PAHs in biochar briefly summarized the two main formation pathways, namely diels-alder condensation and free radical reaction (Han et al., 2022; Odinga et al., 2021; Wang et al., 2017). However, comprehensive formation pathways (such as free radical addition pathways) of PAHs are inadequately understood based on existing literature. Therefore, it is necessary to comprehensively summarize the formation mechanisms of PAHs in biochar, which could help reduce and control the formation of PAHs.

Currently, most of the studies mainly focus on how to reduce the content of PAHs in biochar by changing the pyrolysis conditions (Devi and Saroha, 2015; Konczak et al., 2019; Zhang et al., 2019). For instance, increasing the flow rate of carrier gas or changing the type of carrier gas can reduce the content of PAHs in biochar (Konczak et al., 2019; Madej et al., 2016). In addition, several studies have proposed mitigation strategies for PAHs in biochar, including pyrolysis treatment, chemical modification, and co-pyrolysis (Kołtowski and Oleszczuk, 2015; Zhao et al., 2020). Although these methods can reduce the total content of PAHs in biochar, the content of other kinds of PAHs may also increase depending upon the treatment processes. For example, after pyrolysis of iron-loaded biomass, although the total content of PAHs in biochar was reduced, the production of more toxic 5-ring and 6-ring PAHs increased, which resulted in higher toxicity of biochar (Zhao et al., 2020). It has been reported that sunlight irradiation can increase the content of 3-ring and 4-ring PAHs in biochar, but reduce the total concentration of PAHs (Khalid and Klarup, 2015). However, it is unclear whether these methods can be widely used for the treatment of biochar and the impact on animals and plants after biochar treatment. Therefore, to solve the above issues, it is necessary to systematically summarize the formation of PAHs in biochar and its influencing factors, content distribution, risk assessment, current research status, and progress of existing methods for degradation.

Based on the above reasons, the objectives of this review are to (1) summarize the formation mechanisms, influencing factors, and potential risk assessment methods of PAHs in biochar; (2) analyze the most effective ways for minimizing the formation of PAHs in biochar; (3) propose perspectives and suggestions for the future studies. This review provides a guide for reducing the formation of biochar-associated PAHs and their toxicity, which is beneficial for the development and large-scale safe use of environmentally friendly biochar.

2. Methods of literature search

To have a comprehensive grasp and understanding of current literature related to PAHs in biochar, this paper mainly searched the literatures published in the Web of Science and PubMed. Keywords mainly include “biochar,” “polycyclic aromatic hydrocarbons,” “hydrothermal charcoal,” and “review,” using the combination of “and” and “or”, and manually screening the searched literature. The relevant studies were obtained after a manual selection was carried out to avoid inconsistent references, which can be automatically found after the document search. As shown in Fig. 1, in the past 10 years, the research on PAHs in biochar has shown an overall upward trend in recent years. Meanwhile, to more intuitively demonstrate the research hotspots of PAHs in biochar, a semiquantitative assessment was performed using the VOSviewer (https://app.vosviewer.com/) software. As shown in Fig. 2, the thickness of the lines increases with the strength of the correlation among the keywords. It can be seen that PAHs are closely linked to biochar and mitigation measures.

To better distinguish the types of biochar, it is classified based on the source of feedstocks. The biochar feedstocks were generally divided into agricultural waste (wheat straw, rice straw, maize straw, maize, rice husk, corn straw, potato straw, soybean straw, corn, walnut shells, wheat straw, cotton straw, coconut shells, wheat husk, rice husk, and grass), woody waste (sawdust, conifers, reed, *Picea abies*, *Populus tremula*, pine, woodchip, hardwood, wood, wood waste, wood dust, and willow), green waste (*Arundo donax,* bamboo, sugarcane, coconut, *Miscanthus*, leaves, vineyard pruning waste, and olive pomace), industrial waste (sewage sludge, distillers grains, dairy processing sludge, anaerobically digested sewage sludge, paper sludge), poultry manure (pig manure, cow manure, chicken manure, swine manure, bone meal, and co-digested cow manure) and food waste (coffee ground, vegetable waste, and nut). The pyrolysis temperatures used for the preparation of biochar were classified as low (300–500 °C), medium (500–600 °C), and high (600–800 °C). The pyrolysis type is slow pyrolysis and the carrier gas type is N_2. The data in the tables were taken directly from the articles. In addition, the data presented as images were extracted using the GetData graphical digitizer software (http://getdata-graph-digitizer.com/).

3. Distribution of PAHs and their content in biochar

3.1. Distribution of PAHs in solid, liquid, and gas phases

During the pyrolysis process, PAHs are formed through aromatization, cyclization, and other pathways, which are distributed in bio-gas, bio-oil, and biochar (Fig. 3). To understand the distribution law of PAHs generated during biomass pyrolysis, some studies have measured PAHs in bio-oil or syngas generated during the preparation of biochar

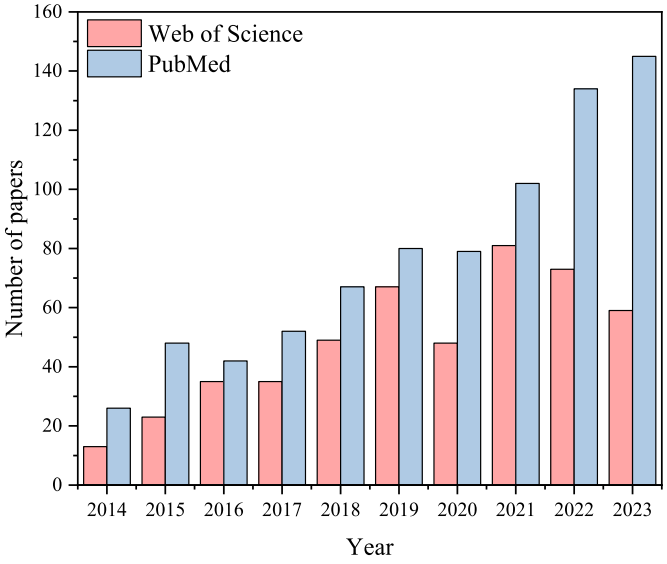


Fig. 1. Publications over time by analyzing the keywords “biochar” and “polycyclic aromatic hydrocarbons” through the Web of Science and PubMed database.

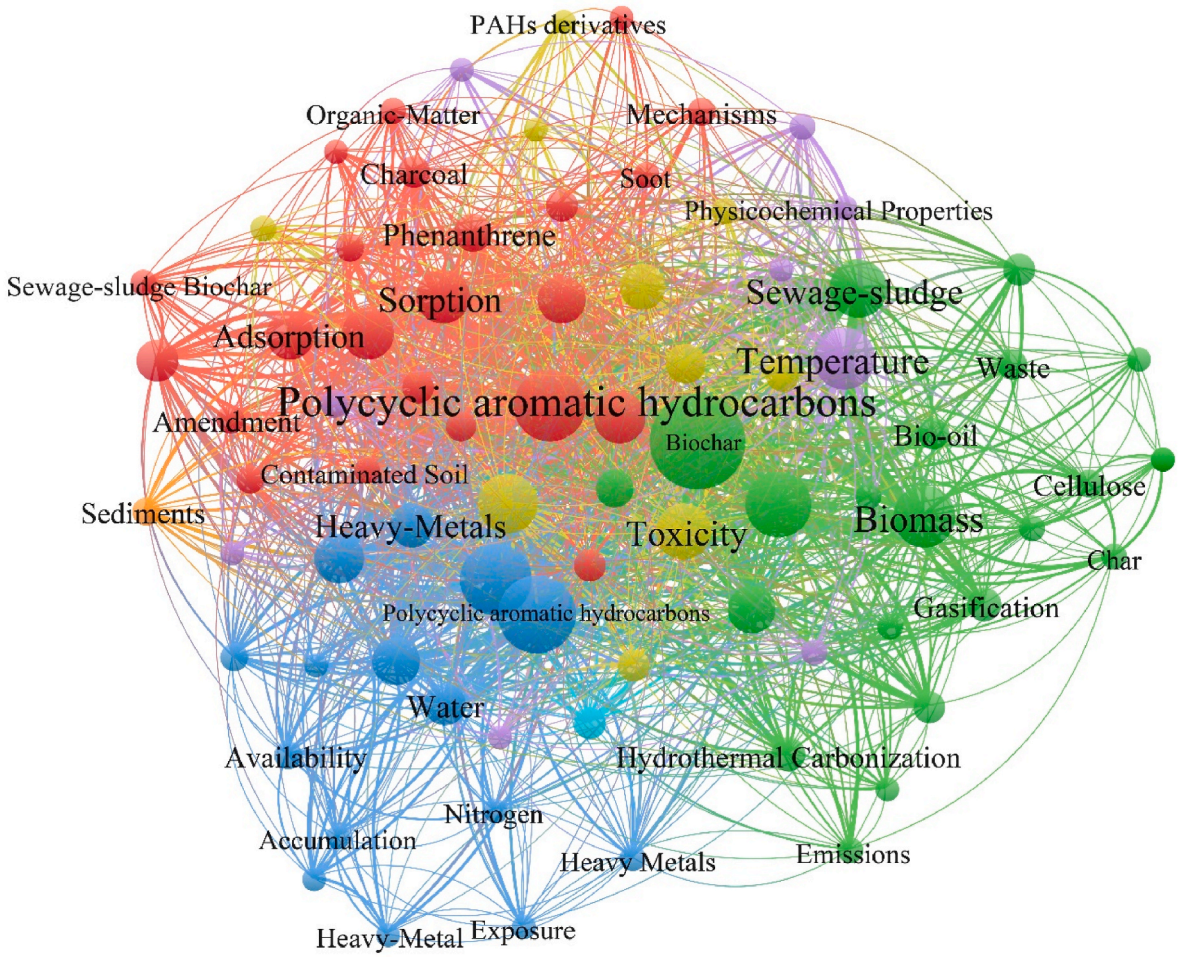


Fig. 2. Semiquantitative assessment of the data collected from the Web of Science and PubMed database performed via the VOSviewer software. (The size of the circle in the figure indicates the frequency of keyword occurrence, and the larger the circle, the more keywords appear. The line in the figure represents the connection strength of the keyword, which is the total number of times the keyword co-occurs with other keywords. The higher the connection strength among the co-occurred keywords, the greater their influence in the co-occurrence network.)

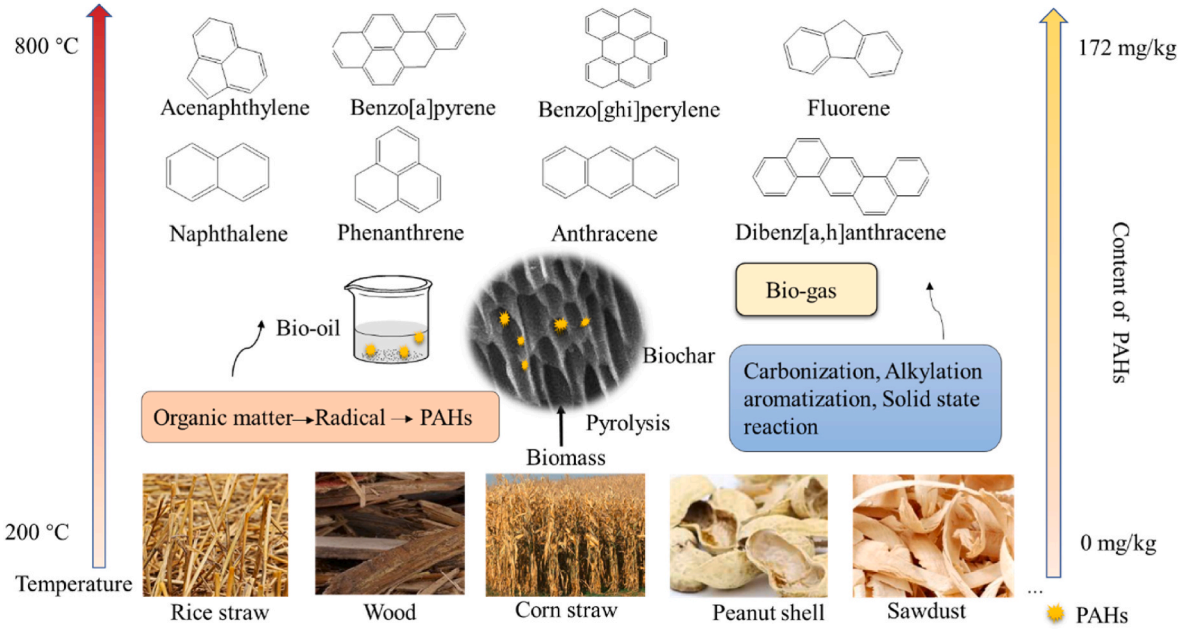


Fig. 3. The formation process of PAHs during biomass pyrolysis.

(Fagernas et al., 2012; Nguyen et al., 2019; Zhao et al., 2020). Choosing appropriate extraction methods and extractants is crucial for the determination of PAHs. Generally, the extraction methods for PAHs in biochar include accelerated solvent extraction, Soxhlet extraction, ultrasound extraction, microwave extraction, etc. In addition to different extraction methods, there are also various extraction solvents, such as toluene, n-hexane, cyclohexane, acetonitrile and toluene, acetonitrile and n-hexane, dichloromethane and acetone, and a mixed solvent of dichloromethane and ethanol (Wang et al., 2017). In general, PAHs in biochar are extracted and determined by the method recommended by European Biochar Certificate (EBC), including Soxhlet extraction with toluene as solvent, and then analyzed by gas chromatography-mass spectrometry (EBC, 2015; Hale et al., 2012). Bio-oil and bio-gas were collected with isopropanol and concentrated for determination (Zhao et al., 2020).

During biochar preparation, PAHs were mainly distributed in bio-oil and a small part in biochar and syngas (Shen et al., 2022). For instance, previous studies showed that most PAHs were concentrated in the bio-oil portion (72.70%–94.60%), and only a small part was retained in biochar (1.70%–11.10%) and syngas (2.20%–16.20%) (Zhao et al., 2020). Besides Fagernas et al. (2012) also found that 62.00%, 37.00%, and 0.60% of PAHs were distributed in tar, syngas, and biochar, respectively. Thus most PAHs enter the bio-oil and only a small PAHs are in biochar, which may be due to the presence of hot gas flow and carrier gas.

Gas emitted from the production of charcoal contained significant amounts of PAHs with an average total concentration of 18–34 μg/m^3 (Bucheli et al., 2015; Mara dos Santos Barbosa et al., 2006). The average concentration of PAHs in agricultural waste tar produced by rapid pyrolysis (500 °C) was 3.3–12.7 mg/L. Maize straw, poplar, and willow branches were slowly pyrolyzed at 650 °C for 30 min, providing the content of PAHs of about 28–183 mg/kg (wet weight) in the bio-oil (Cordella et al., 2012). To be used as recyclable fuels, bio-oil needs further improvement because PAHs in it can transport into the environment.

Since 2010, several articles have been published on the concentration of PAHs in biochar from different feedstocks when subjected to various pyrolysis conditions (Devi and Saroha, 2015; Lyu et al., 2016; Zielinska and Oleszczuk, 2016). Table S1 summarizes the concentration of PAHs in biochar from various feedstocks at different pyrolysis temperatures, ranging from 0 to 172 mg/kg. Thus, PAHs content in biochar fluctuates largely depending on production parameters. In addition to the parent PAHs, biochar may also contain more toxic PAHs derivatives (such as O-PAHs and N-PAHs) (Krzyszczak et al., 2021, 2023; Krzyszczak Turczyn et al., 2024). As shown in Table S2, the content of PAHs derivatives in biochar produced from sludge, willow, cork, wheat straw, and bio-gas residue at pyrolysis temperatures of 500–700 °C is 2.72–5300, 1.92–4310, 11.89–111890, 19.16–2840, and 3.42–28390 ng/g, respectively. However, the contents of PAHs derivatives in wood biochar are below the detection limit, indicating that wood-derived biochar has relatively lower contents of PAHs derivatives than other biochars. Overall, the content of PAHs in biochar is highly variable, which depends on the feedstocks and pyrolysis conditions.

3.2. Bioavailability of PAHs in biochar

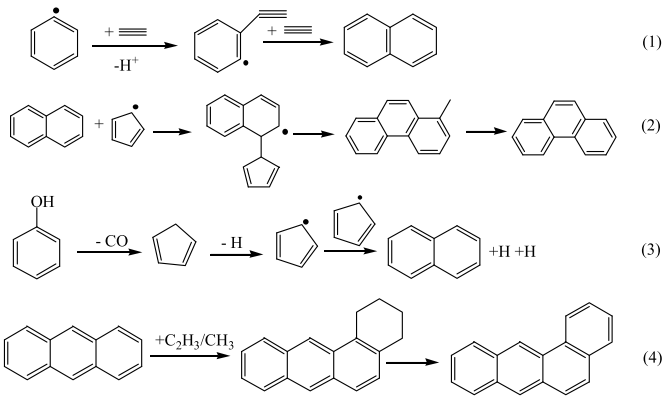
Bioavailability of PAHs can be absorbed by plants, animals, and microorganisms, and transferred through the food chain, resulting in risks to human health (Sun et al., 2022; Yang et al., 2019). Therefore, it is essential to quantify the concentration of bioavailable PAHs and their derivatives. For instance, Hale et al. (2012) used polyoxymethylene passive samplers to determine the bioavailable PAHs concentration in biochar from 23 different biomass. The concentration of bioavailable PAHs in biochar ranged from 0.17 to 10 ng/L. Hilber et al. (2017) determined the concentration of bioavailable PAHs in biochar derived from wood, *Miscanthus*, sugar beets, green waste, sludge, and the ranges of concentration are 12–81 ng/L. It has been reported that these PAHs inhibit the growth of the roots of *L. sativum*, even with a low PAHs content (90.38 ng/L) (Zielinska and Oleszczuk, 2016). As shown in Table S2, the bioavailability of PAHs derivatives in biochar is one order of magnitude lower than the content of derivatives, ranging from below the detection limit to 1.90 ng/L. Overall, the content of bioavailable PAHs in biochar is very low, but their toxicity cannot be ignored. Phytotoxicity exhibited a significant positive correlation with the concentration of bioavailable PAHs in biochar (Shen et al., 2022). Furthermore, when biochar is used for environmental remediation, PAHs could be desorbed from biochar because the bioavailability of PAHs is affected by dissolved organic matter, surfactants, microorganisms, and other factors. This could improve their bioavailability and toxicity (Wang et al., 2017). Therefore, more future studies are needed to explore the bioavailability and toxicity of PAHs in biochar.

4. Formation mechanisms and influencing factors of PAHs in biochar

In recent years, the formation mechanisms of PAHs during biomass pyrolysis have been studied. Although the existing knowledge about the formation mechanisms of PAHs are still limited, some important findings have been well summarized in recent studies (Mayer et al., 2016; Wang et al., 2017). For instance, pyrolysis temperature is an important factor affecting the formation of PAHs. At low temperatures, PAHs were mainly formed by aromatization and cyclization. At high temperatures, PAHs were formed by hydrogen extraction acetylene addition (HACA) (Wang et al., 2017). However, the formation mechanisms of PAHs in biochar are relatively scattered. Thus, summarizing the formation mechanisms of PAHs in biochar could contribute to the control of PAHs production during pyrolysis and the safe utilization of biochar.

4.1. Formation mechanisms of PAHs in biochar

Macromolecular depolymerization and carbonization of biomass reactions occur during the thermochemical conversion process. There are various formation mechanisms of PAHs during the pyrolysis of feedstocks. In general, during the thermochemical conversion process, PAHs formation mechanisms can be divided into HACA and free radical reactions (Reizer et al., 2022). HACA is a recognized mechanism for the formation of PAHs (Liu et al., 2017; Ye et al., 2022). For example, phenylacetylene is formed from benzene and then continues to the formation of naphthalene according to Eq. (1). Therefore, monoaromatic compounds such as styrene and benzene are considered as the main precursors for PAHs formation.



Mechanisms for the formation of PAHs through radical reactions include radicals-methyl addition cyclization (MAC), ethynyl radical,

phenyl addition cyclization (PAC), and resonantly stabilized radicals reaction pathway (Reizer et al., 2022). The lignocellulose feedstocks are cracked to form different gaseous hydrocarbon radicals, such as acetylene (CH≡C−), 1,3-butadiene, propargyl (C_3H_3), and cyclopentadienyl (C_5H_5). These radicals undergo a continuous series of reactions to form a larger (poly)aromatic ring structure, similar to the mechanism of dehydrogenation of acetylene (Eq.4). At pyrolysis temperatures below 500 °C, PAHs are mainly formed by monomolecular cyclization, dehydrogenation, dealkylation, and aromatization of volatile substances (Bucheli et al., 2015). During pyrolysis, lignin, cellulose, and lipids (resins and steroids) undergo cyclization, dehydrogenation, dealkylation, and aromatization, forming PAHs (Kaal et al., 2012). Raising the pyrolysis temperature from 500 to 950 °C enhances the secondary cracking of bio-oil, producing highly active free radicals (such as acetylene and 1,3-butadiene). Then these free radicals are thermally synthesized into aromatic structures, and then HMW PAHs are formed through the "zigzag addition process." Some lipids in biomass, such as rosin acid and pimaric acid, would be dehydrogenated to form pyroxene (1-methyl-7-isopropylphenanthrene) and pimsonene (1,7-dimethylphenanthrene) during pyrolysis. These alkyl-substituted PAHs can be formed by a dealkylation reaction (Ramdahl, 1983; Zhou et al., 2014). Propargyl (C_3H_3) and cyclopentadienyl (C_5H_5) can be rearranged to obtain the final product benzene and naphthalene, respectively (Richter and Howard, 2000). Biphenyl generates triphenylene through the PAC mechanism (Zhao et al., 2019). In addition, C_4H_4 successfully facilitates PAHs formation reactions, and the corresponding mechanism is called hydrogen abstraction vinyl acetylene addition (HAVA) (Yang et al., 2015). In the HAVA mechanism, after a PAHs radical is formed, through HAVA, it is dehydrogenated and cyclized to form new PAHs (Reizer et al., 2022; Ye et al., 2022).

Regarding the formation of PAHs in iron-modified biochar, another pathway based on the reaction of naphthalene and cyclo-pentadiene has been proposed for the formation of PAHs (Eq.2, Eq.3) (Zhao et al., 2020). In conclusion, PAHs in biochar are mainly formed by HACA, cyclization, and MAC mechanisms. Although some reaction mechanisms have been explored, due to the complexity and diversity of PAHs, the formation mechanisms of PAHs are still unclear. It is not clear which mechanisms are dominant and what the contribution rate is, which needs further in-depth study.

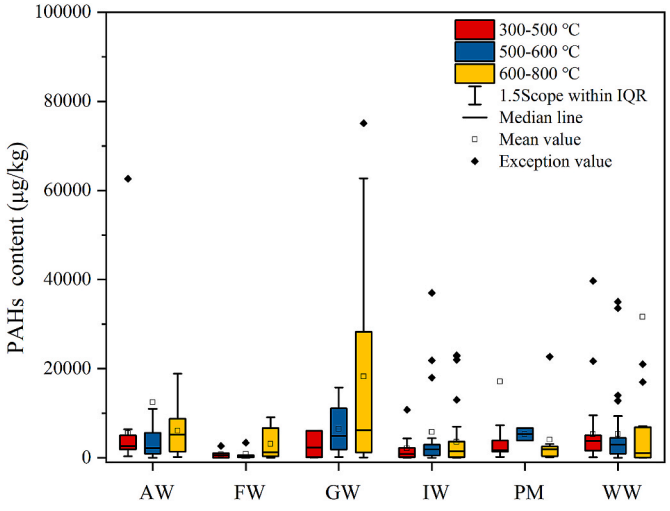


Fig. 4. Relationship between feedstock and PAHs content in biochar. (The pyrolysis type is slow pyrolysis. AW: agricultural waste, FW: food waste, GW: green waste, IW: industrial waste, PM: poultry manure, WW: woody waste. Data from Web of Science and PubMed).

4.2. Influencing factors for the formation of PAHs

The formation of PAHs in biochar is affected by various factors, such as feedstocks, pyrolysis temperature, and carrier gas. Therefore, the extraction methods and pyrolysis conditions should be noted when comparing PAHs content in biochar. The content and abundance of PAHs in biochar obtained from different feedstocks and pyrolysis conditions are considerably different (De la Rosa et al., 2019). For example, many studies have shown that the most abundant PAHs in biochar are typically naphthalene (or naphthalene and phenanthrene), while LMW-PAHs account for the majority of the total content (Hale et al., 2012; Yang et al., 2021).

4.2.1. Feedstocks

Feedstock is one of the factors that affect the content of PAHs in biochar. The types and properties of feedstocks, as well as their composition, may lead to differences in the content of PAHs. The relationships between feedstocks and PAHs content in biochar are shown in Fig. 4. PAHs content exhibited an order of green waste biochar>agricultural waste biochar>poultry manure biochar>woody waste biochar>industrial waste biochar>food waste biochar at a pyrolysis temperature of 500–600 °C. It can be confirmed from Fig. 5 that the PAHs contained in agricultural waste, woody waste and green waste biochar are significantly higher than industrial waste, poultry manure and food waste biochar at the pyrolysis temperature of 600 °C. The content of PAHs in food waste biochar at 600 °C was lower than those of the other five types of feedstocks. Therefore, feedstocks have a significant effect on the content of PAHs in biochar. Selecting suitable feedstocks could help to reduce the content of PAHs in biochar. Based on the total concentration of PAHs, it has been suggested that food waste biochar may be a promising feedstock for the preparation of biochar.

Some studies have found that biochar prepared at 500–600 °C contains more PAHs in agricultural waste biochar (especially straw biochar) than wood biochar (Krzyszczak et al., 2023; Qiu et al., 2015; Wang et al., 2018b). For example, Buss et al. (2016) found that the concentration of PAHs in rice straw biochar was 5.8 times higher than that of cork biochar. Compared with straw, wood usually has a higher lignin content (Trubetskaya et al., 2016; Zhang et al., 2022a). In general, biochar prepared from lignin-rich feedstocks contains less PAHs compared with pectin and cellulose-based feedstocks (De la Rosa et al., 2019; Ramesh K. Sharma and Hajaligol, 2003). For biomass rich in lignin, pectin, and xylan, the formation of PAHs may follow the same route as benzene as

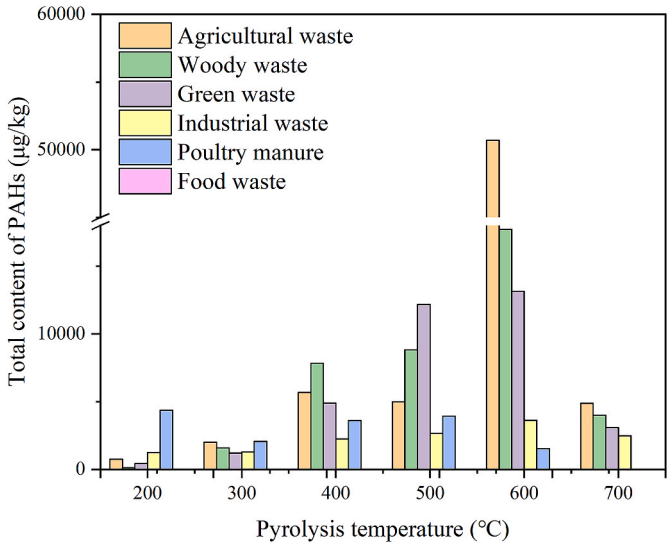


Fig. 5. The relationship between PAHs and pyrolysis temperatures in biochar from different organic solid wastes. (Data from Web of Science and PubMed)

Table 1
Basic physical and chemical properties of biochar.

Feedstocks	Pyrolysis temperature (°C)	Ash (wt%)	C (wt%)	H (wt%)	O (wt%)	N (wt%)	PAHs content (mg/kg)	References
Vegetable waste	200	16.59	41.05	5.35	27.96	3.26	3.30	Yang et al. (2019)
Vegetable waste	500	36.67	48.21	1.99	10.85	3.49	3.40	Yang et al. (2019)
Pine cones	200	0.77	62.50	1.91	24.28	0.93	6.93	Yang et al. (2019)
Pine cones	500	8.96	73.11	2.56	20.51	1.77	1.61	Yang et al. (2019)
Paper mill sludge	200	–	20.72	2.74	31.23	0.35	0.32	Zhang et al. (2015)
Paper mill sludge	300	–	21.14	2.57	29.26	0.33	0.32	Zhang et al. (2015)
Paper mill sludge	400	–	23.37	1.93	25.81	0.32	5.96	Zhang et al. (2015)
Paper mill sludge	500	–	24.98	1.24	19.97	0.98	16.92	Zhang et al. (2015)
Paper mill sludge	600	–	25.13	0.59	19.30	0.41	0.94	Zhang et al. (2015)
Paper mill sludge	700	–	25.66	0.44	18.45	0.40	0.14	Zhang et al. (2015)
Wheat straw	600	19.59	85.72	1.66	1.26	11.36	0.15	Krzyszczak et al. (2022a)
Willow	600	7.09	82.77	2.24	1.68	9.53	0.18	Krzyszczak et al. (2022a)
Sunflower	600	4.42	81.29	1.58	1.03	11.61	0.15	Krzyszczak et al. (2022a)
Sewage sludge	600	67.60	26.5	0.60	2.93	2.41	0.12	Krzyszczak et al. (2022a)
Sewage sludge	600	70.27	23.72	0.44	3.29	2.29	0.19	Krzyszczak et al. (2022a)
Sewage sludge	600	63.58	24.45	0.86	2.24	8.84	0.15	Krzyszczak et al. (2022a)
Sewage sludge	600	63.86	27.68	0.82	3.76	3.89	0.13	Krzyszczak et al. (2022a)
Sewage sludge	450	–	38.02	2.22	3.51	5.04	29.62	Ma et al. (2021)
Sewage sludge	600	–	31.07	1.15	6.12	4.59	1.43	Ma et al. (2021)
Cornstalk	600	18.18	57.90	4.02	1.58	18.25	9.34	Shen et al. (2022)
Peanut shell	600	12.45	67.67	3.54	2.79	13.49	17.10	Shen et al. (2022)
Rice husk	600	39.53	49.92	1.73	0.69	8.07	17.24	Shen et al. (2022)
Pig manure	425	55.61	29.3	2.37	–	4.00	0.19	Wystalska et al. (2023)
Pig manure	525	63.91	29.16	1.56	–	3.26	0.13	Wystalska et al. (2023)
Pig manure	625	63.50	35.78	1.17	–	3.03	2.11	Wystalska et al. (2023)
Pig manure	725	73.34	32.47	1.36	–	3.02	22.69	Wystalska et al. (2023)
Chicken manure	400	–	44.80	2.60	–	4.40	3.93	Frišták et al. (2019)
Chicken manure	500	–	46.30	1.60	–	4.10	3.92	Frišták et al. (2019)
Pig manure	400	34.28	38.52	2.17	21.29	2.86	1.38	Zhang et al. (2023)
Pig manure	600	52.73	24.16	1.48	18.82	2.16	0.38	Zhang et al. (2023)
Cow manure	400	50.68	26.73	2.02	18.53	1.62	1.75	Zhang et al. (2023)
Cow manure	600	65.82	18.31	1.12	13.21	1.08	2.01	Zhang et al. (2023)
Coffee ground	300	–	83.90	–	11.90	4.20	0.56	Nguyen et al. (2019)
Coffee ground	500	–	87.80	–	10.70	1.50	0.59	Nguyen et al. (2019)
Coffee ground	700	–	85.70	–	10.70	3.60	0.71	Nguyen et al. (2019)
Coffee ground	900	–	85.20	–	11.00	3.80	0.85	Nguyen et al. (2019)

intermediates. PAHs may grow through the HACA mechanism or naphthalene interaction (Zhou et al., 2015). In addition, lignin is more likely to produce PAHs through resonance-stabilized hydrocarbon-radical chain reaction than cellulose and hemicellulose (Wang et al., 2023). The interaction between biomass components is a relatively complex process, especially the influence of PAHs formation. Therefore, further studies should be carried out to focus on the influence of biomass interaction and the formation mechanisms of PAHs.

Furthermore, the concentration of PAHs and the content of ash, carbon, hydrogen, oxygen, and nitrogen in biochar are shown in Table 1. It was observed that the increase in ash content promoted the increase of PAHs concentration in pig manure biochar, which indicated that ash and inorganic compounds affect the formation of PAHs (Krzyszczak et al., 2021). Ash can be used as a catalyst in the formation of PAHs or a precursor of HACA, promoting the formation of LMW-PAHs (Richter and Howard, 2000). With the decrease in the C/H ratio, the content of PAHs in biochar gradually increased. On the contrary, some studies showed that the content of PAHs also increased with the enhancement of the C/H ratio. For instance, Qiu et al. (2015) observed that the highest concentration of PAHs in plant residues was prepared at 450 °C, while the total concentration of PAHs in animal waste biochar at 450 °C was usually lower than that in animal waste biochar prepared at 300 °C and 600 °C. The presence of higher mineral content accelerated the depolymerization of organic matter, which promoted the high yield of PAHs. Therefore, it is still very challenging to predict the concentration of PAHs in biochar based on the composition of feedstocks.

4.2.2. *Pyrolysis temperatures*

The relationship between pyrolysis temperature and PAHs content is presented in Fig. 5. There are few studies on PAHs in poultry manure and food waste biochar, especially the pyrolysis temperature of 700 °C (Fig. 5). As shown in figure, most biochar prepared at 500–600 °C had relatively high content of PAHs, which was consistent with the study of Devi and Saroha (2015). Compared to other pyrolysis temperatures, the content of PAHs in agricultural waste biochar and woody waste was the highest at 600 °C. As the pyrolysis temperature increases, organic compounds (including aliphatic and aromatic components) in wood undergo pyrolysis. PAHs enhance thermal conversion through aromatization, dehydrogenation, dealkylation, and degradation, which further affects the yield of PAHs pyrolysis products (Sørmo et al., 2024). The content of PAHs in some biochar increased with the increase in pyrolysis temperature. However, the total content of PAHs in biochar decreased with the increase in temperature (Eugenia Gonzalez et al., 2017; Hung et al., 2024). The results of this study were very similar to the changes of PAHs in straw biochar (Wang et al., 2018b), which were opposite to the findings of a previous study carried out on wood biochar (Kloss et al., 2012). The trend of PAHs content in biochar with pyrolysis temperature variations was not consistent in the literature. Therefore, it is difficult to accurately determine which pyrolysis temperature is the most suitable for producing the safest biochar for potential environmental applications. However, the statistical results showed that the content of PAHs in most biochar increased first and then decreased with the increase of pyrolysis temperature. At 500–600 °C, the content of PAHs in most biochar is relatively high. It is suggested that agricultural waste, wood waste and green waste biochar should be produced above 700 °C to obtain biochar with low PAHs content.

Temperature also affects the abundance of different PAHs. In some studies, when the pyrolysis temperatures increase, the concentration of LMW-PAHs in biochar decreases, and the concentration of medium and HMW-PAHs increases (Weidemann et al., 2018; Zhang et al., 2019). For example, Dunnigan et al. (2017) observed that increasing the pyrolysis temperature from 400 to 800 °C increased the content of benzo[a]

pyrene in finely ground rice husk biochar produced in a continuous pyrolysis-combustion system. LMW-PAHs (naphthalene, phenanthrene) dominate in biochar, while HMW-PAHs are relatively rare (Greco et al., 2021; Wang et al., 2018b). It was noticed that the concentration of naphthalene increased with the rise in pyrolysis temperature. This may be attributed to the fact that the aromatization and pyrolysis reactions result in the synthesis of 4-ring to 6-ring PAHs at high temperatures, and the partial cleavage of HMW-PAHs into relatively stable LMW-PAHs, such as naphthalene. Its composition mainly changes towards the form of naphthalene, while the possibility of other PAHs decreases. Moreover, Kloss et al. (2012) proved that the abundance of PAHs in biochar increases with the increase in pyrolysis temperature. This was assigned to the predominance of 2-ring and 3-ring in biochar. The increase in temperature enhanced the aromaticity of the biochar surface and the binding force between PAHs and biochar. Therefore, the binding power between PAHs and biochar was higher, while the bioavailability of PAHs was lower due to the larger hydrophobicity and π-π electron donor-acceptor interaction strength.

Pyrolysis temperature is an important factor affecting the toxicity of biochar. Konczak et al. (2020) observed increased toxicity of sludge biochar against *Candida* with increased pyrolysis temperature. The removal of PAHs may be due to their volatilization into the gas phase and thermal degradation during pyrolysis. In addition, Wang et al. (2013) suggested that PAHs in low-temperature biochar exert a suppressing effect on N_2O emissions, whereas PAHs in high-temperature biochar have no effects on N emissions. Hence, reducing PAHs content in biochar is also beneficial for the emission reduction of N_2O. These findings endorsed that pyrolysis temperature is one of the critical factors affecting PAHs in biochar. Biochar produced at higher temperatures exhibited low toxicity and environmentally friendly characteristic.

4.2.3. Carrier gas

It has been confirmed that carrier gas significantly affects the content of PAHs in biochar. For example, Buss et al. (2016) revealed that the concentration of PAHs in biochar reduces with an increase in carrier gas flow rate (0, 0.33, and 0.67 L/min) by controlling the pyrolysis conditions. For the same pyrolysis temperature and residence time, when the carrier gas flow rate was 0 and 1.0 L/min, the PAHs concentration difference in the two biochars was about 6 μg/kg. The flow rate of the carrier gas would affect PAHs concentration in biochar. Therefore, choosing a high flow rate of carrier gas is suggested to obtain safe biochar. In addition, the type of carrier gas also affects the formation of PAHs in biochar (Godlewska and Oleszczuk, 2022; Konczak et al., 2019). The percentage of 3–6 rings PAHs in sludge biochar prepared in a CO_2 atmosphere was lower prepared in an N_2 atmosphere (9.00%–62.80%) (Konczak et al., 2019). In the future, CO_2 may serve as the optimal carrier gas for pyrolysis medium and establish an environmentally friendly and energy-saving process.

4.2.4. Other factors

Besides feedstock type, pyrolysis temperature, and carrier gas flow rate, many other relevant factors, including residence time, pyrolysis rate, and pyrolysis reactor design also influenced the content of PAHs in biochar. Many studies also showed a tendency to decrease PAHs concentration in biochar with increasing residence time for pyrolysis (Hale et al., 2012). When the pyrolysis temperature is above 600 °C and the residence time is more than 30 min, the prepared sludge biochar can remove most PAHs (Mosko et al., 2021). Similarly, Kloss et al. (2012) observed slightly lower concentration of PAHs in biochar at a residence time of 10 h compared to 5 h. The types of pyrolysis reactors included conventional kilns, batch reactors, and rotary reactors. Due to uncontrolled temperature, biochar production using conventional kilns can contain large amounts of PAHs (Buss et al., 2022). Using a batch reaction setup, bio-gas and bio-oil fractions can be separated from the solid phase to avoid condensation of thermally cracked products on the surface of the biochar. The batch reactors can reduce the concentration of PAHs in biochar to meet the quality standards of EBC (2015) and IBI (2015). Therefore, biochar prepared by a batch reactor with a phase separation system has high safety (De la Rosa et al., 2019). It has been suggested that regardless of the feedstock or temperature, the rotary reactor can produce the safest biochar (Buss et al., 2016). Therefore, biochar with low PAHs content can be produced by selecting rotary reactors as pyrolysis devices.

Few studies are available regarding the influence of O_2 on the concentration of PAHs in biochar. For example, pyrolyzed *Miscanthus* in an N_2 stream containing 0.50%, 1.00%, and 2.00% of O_2, and the results showed that the oxygen content had no significant influence on the PAHs content in biochar (Madej et al., 2016). The PAHs concentration in the biochar from *Miscanthus* and sieved coniferous wood residue did not change significantly when the O_2 content increased. However, the concentration of PAHs in the sugar beet biochar produced under enhanced O_2 environment significantly increased (Hilber et al., 2017). Therefore, it was also suggested that O_2 should be kept to a minimum level to reduce the production of PAHs.

5. Application risk assessment of biochar containing PAHs

Risk assessment is an essential part in the life cycle assessment of biochar. Risk assessment can determine whether biochar can be sustainably used on a large scale. When PAHs containing biochar is used for environmental remediation, it may pose risks to the environment (Wang et al., 2019b). Hence, it is necessary to assess the risk of biochar application. Commonly used risk assessment methods were reviewed in this section.

5.1. Total content of PAHs

The total concentration of PAHs in biochar is one of the evaluation indicators to assess environmental risk. The total content threshold of PAHs in biochar set by IBI is 6–20 mg/kg (IBI, 2015), and the threshold set by EBC is 4–12 mg/kg (EBC, 2015). Research has shown that when biochar is used as a soil conditioner or fertilizer, biochemical processes in soil may change the physicochemical properties of biochar, which may lead to the release of blocked PAHs (Krzyszczak Turczyn et al., 2024). Therefore, PAHs in biochar are introduced into the soil as a potential source. In general, even if the concentration of PAHs in biochar meets the IBI and EBC standards, adding these kinds of biochar to soil still seems to have potentially adverse risks (Wang et al., 2019b). Therefore, based on the total content of 16 PAHs (ΣPAHs), it is impossible to assess the environmental risk of PAHs in biochar comprehensively. The total content of PAHs can only be used as a preliminary indicator. In future research, the safety of biochar can be comprehensively evaluated according to PAHs content and the toxic equivalents value.

5.2. Toxic equivalents

One of the current methods commonly used for the risk assessment of PAHs is the toxic equivalence method, which was adopted in many studies (Devi and Saroha, 2015; Dunnigan et al., 2017; Zhao et al., 2020). The important concept of toxic equivalent factor (TEF) has been introduced because carcinogenicity differs among different species of PAHs. Commonly, benzo[a]pyrene is chosen as a reference compound because of its strong carcinogenicity to humans, which has been given a TEF value of 1, and the TEF values for the rest of the 15 PAHs were determined based on their relative benzo[a]pyrene. The carcinogenicity values of pyrene are shown in Table S3. Taking into account that the abundance of different species of PAHs also varies, the toxic equivalents (TEQ) of PAHs can be calculated according to Equation (5).

$$TEQ = \sum (PAH_i \times TEF_i) \quad (5)$$

where PAH_i is the concentration of the ith PAH_i (mg/kg). TEF_i is the toxic equivalence factor for the ith PAH (Tsai et al., 2009). As light and low toxic PAHs are dominant in biochar, TEF may be more suitable for ecotoxicological risk assessment of biochar. TEQ can calculate the contribution rate of each pollutant to the overall toxicity, and as a conventional risk assessment method, it could be widely used in future research.

5.3. Ecotoxicological methods

Ecotoxicological methods are often used to assess the environmental risk of biochar. Based on a series of biological experiments with plants, bacteria, protozoa, and crustaceans, some studies have been conducted on the toxicological evaluation of biochar (Gondek et al., 2017; Oleszczuk et al., 2013). For instance, Yang et al. (2019) systematically studied the toxicity of biochar, including in vitro experiments using human liver and lung cells, as well as in vivo experiments using *Drosophila melanogaster*. The results showed that biochar had a limited effect on the viability of *Drosophila melanogaster*, but had a negative effect on the growth of human liver and lung cells under high concentration conditions. Similarly, a study revealed the potential mutagenic effects of PAHs in biochar in the *Ames Salmonella*/microsomal mutagenicity test (Anjum et al., 2014). It has been concluded that compared to the trace metals in the soil, the content of PAHs may pose a real threat, but only for large fleas. Furthermore, there is a significant correlation between the content of PAHs and toxicity to large fleas (Oleszczuk et al., 2013). However, no correlation between PAHs content and toxicities to protozoa and alga was observed in this case. Gondek et al. (2017) also did not find clear evidence that the toxicity of biochar to *Vibrio fischeri* is directly related to the content of PAHs. Therefore, it is difficult to establish a direct relationship between the toxicity of biochar and the level of PAHs.

The application of different concentrations of biochar in the soil produced different levels of PAHs pollution (De La Rosa et al., 2016). For instance, Kuśmierz et al. (2016) observed that the addition of biochar to the soil increased PAHs content in two and a half years of field experiments, and the increase of PAHs was directly proportional to the application amount of biochar. The content of PAHs in soil was increased 10 times by using wooden biochar produced by the traditional kiln method (De La Rosa et al., 2016). Therefore, it is strongly recommended that if biochar obtained from conventional kilns is used as a soil amendment, the biochar must be pretreated to avoid its environmental hazards. In addition, studies have shown the assessment of PAHs intake risk in vegetables by increasing lifetime cancer risk (ILCR) (Zhang et al., 2021). In this study, six kinds of commercial and two kinds of laboratory-prepared biochar were used as soil modifiers to evaluate the accumulation of PAHs in cultivated vegetables grown through greenhouse and field experiments (both biochar application amount was 3.00 wt%). Wang et al. (2018b) observed an increase in the ILCR value of adults exposed to PAHs due to vegetable consumption. It is also found that commercial biochar generally has a higher total concentration of PAHs than that of laboratory-prepared biochar, as well as their toxic equivalents. Also, commercial biochar bioavailable PAHs concentration is higher than that of laboratory-prepared biochar (Oleszczuk et al., 2013; Wang et al., 2018b). Thus, the combination of benzo[a]pyrene toxic equivalents and ILCR is widely used to assess the environmental risk of biochar.

5.4. Other evaluation methods

Currently, there is no ecological risk assessment model and reference-quality value for PAHs in biochar. To assess the potential ecological risk of PAHs caused by the application of biochar to soil, Zhang et al. (2018) used the soil risk entropy method to calculate the minimum and maximum ecological risk entropy of PAHs. When the crop residues are converted into biochar for environmental and agricultural applications, the potential ecological risk of PAHs in biochar is relatively lower when 1.00 wt% of biochar is applied to the soil every year. Furthermore, the risk of PAHs in soil-biochar-plant systems might be predicted using the hydras-1d model (Ma et al., 2021). It was proposed to take the molar ratio of H/C and O/C as the toxicity index of biochar. The larger the ratio, the larger the specific surface area of biochar, and the better the stability of pollutants on biochar (Yang et al., 2019).

Ecotoxicological methods are often used to assess the environmental risk of biochar. These methods can not determine the source of the risk accurately. Therefore, it is suggested that ecotoxicological methods, benzo[a]pyrene toxic equivalents, and ILCR should be combined to evaluate this risk accurately. A complete system has not been formed for the risk assessment of biochar yet. Thus, the environmental risk of biochar needs to be evaluated in depth by other means.

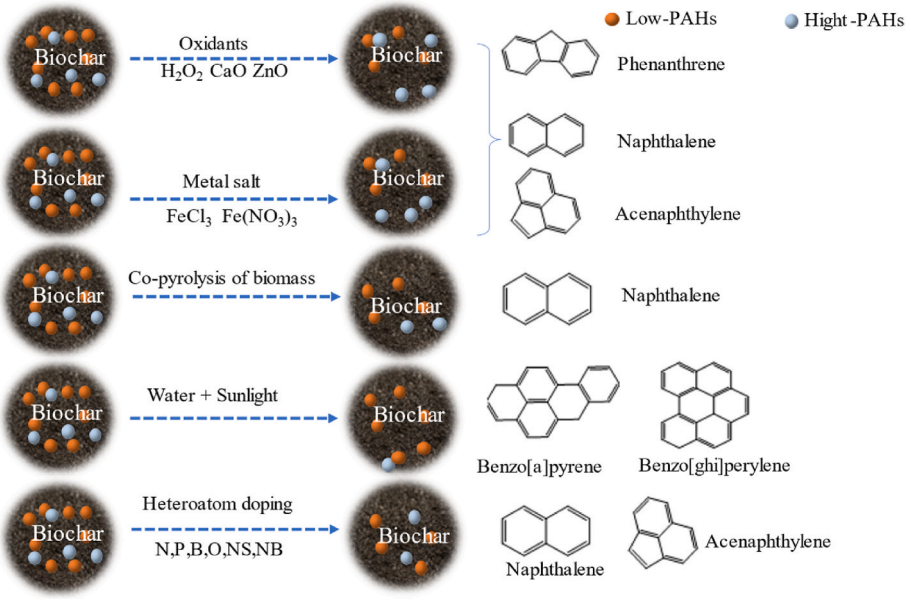


Fig. 6. Reduction of PAHs in biochar by chemical methods.

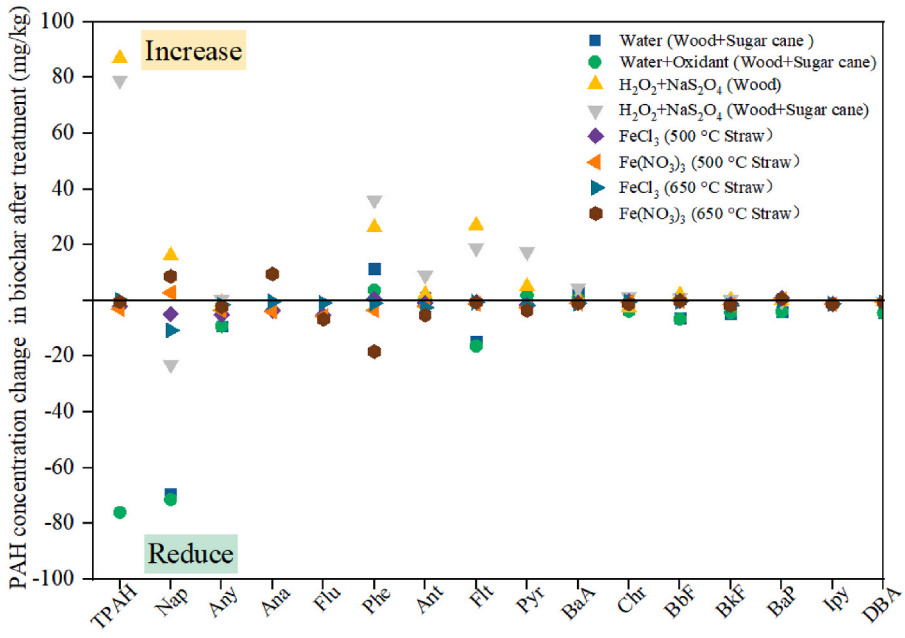


Fig. 7. Changes in PAH composition in biochar after chemical modification (Khalid and Klarup, 2015; Zhao et al., 2020). (TPAH: Total content of PAHs in biochar after chemical modification. Nap: Naphthalene, Any: Acenaphthylene, Ana: Acenaphthene, Flu: Fluorene, Phe: Phenanthrene, Ant: Anthracene, Flt: Fluoranthene, Pyr: Pyrene, BaA: Benze[a]anthracene, Chr: Chrysene, BbF: Benzo[b]fluoranthene, BaP: Benze[a]anthracene, Ipy: Indeno[1,2,3-cd]pyrene, DBA: Dibenz[a,h] anthracene, BPE: Benzo[g,h,i]perylene).

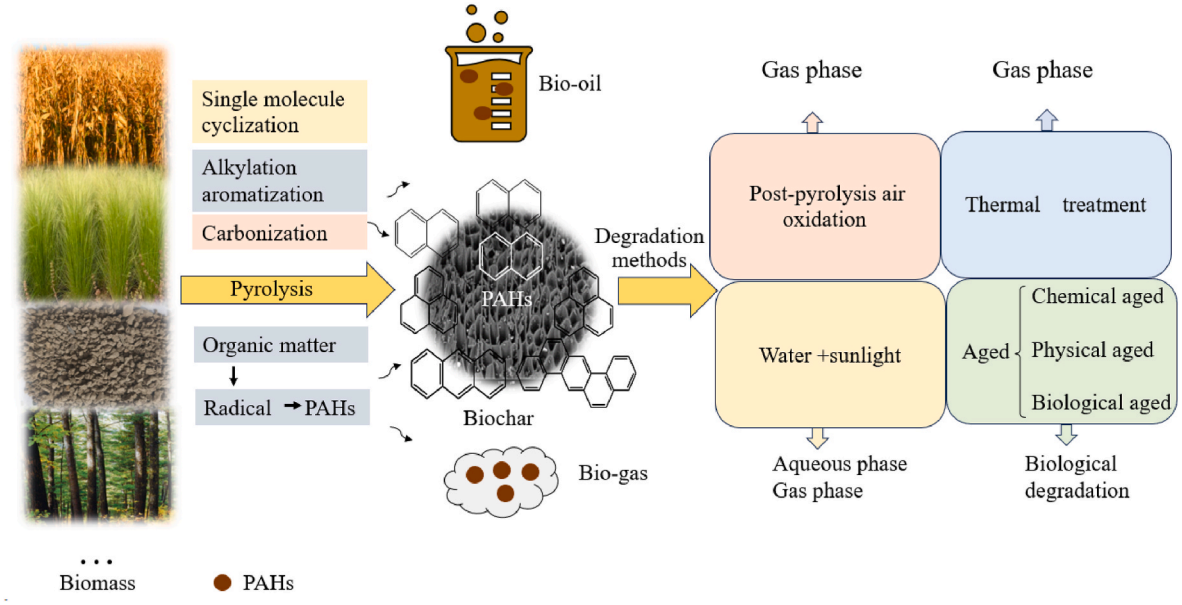


Fig. 8. Formation and destination of PAHs in biochar.

6. Strategies to control PAHs in biochar

For the safe use of biochar, it is essential to control the content of PAHs in biochar. Choosing appropriate pyrolysis conditions can reduce the content of PAHs in biochar. Currently, potential routes, including thermal treatment, thermal oxidation, chemical modification, and biomass co-pyrolysis have also been reported for PAHs degradation in biochar.

6.1. Thermal treatment

Thermal treatment was performed by putting the prepared biochar in an oven at 100–300 °C for 24 h to dry it. Thermal desorption is a classical method for PAHs removal. The prepared biochar usually cools down the heat in a furnace, and this process may remove many PAHs (Han et al., 2022). For instance, Kołtowski and Oleszczuk (2015) thermally treated biochar from elephant grass, willow, and wheat straw produced at 350–650 °C, reducing the PAHs in the biochar by 33.80%–88.10%. Moreover, the content of PAHs in elephant grass biochar decreases the most, depending on the feedstock type. After thermal treatment, the mortality rate of *Daphnia magna* and the toxicity hazard for *Vibrio fischeri* were decreased (Intani et al., 2018; Kołtowski and Oleszczuk, 2015). Similarly, Shi et al. (2021) found that the toxicity of cow dung biochar to earthworms was reduced after thermal treatment, suggesting that

reducing PAHs content reduces its toxicity, which was in agreement with the research results obtained by Kołtowski and Oleszczuk (2015).

Thermal treatment not only change the composition of PAHs in biochar , but also alters the physicochemical properties of biochar. To be specific, the specific surface area and micropore of biochar increased after drying. For example, after thermal treatment, the pH of willow and wheat straw biochar shifts from strongly alkaline to neutral, as shown in Table S4. The PAHs in biochar before drying were dominated by 3–4 rings of PAHs, and the change in the composition of PAHs was noticed after drying (Kołtowski and Oleszczuk, 2015). At 100 °C, most PAHs in biochar were removed. Further increase of drying temperature to 200 °C or 300 °C caused the gradual release of volatile components (Guilloteau et al., 2008). This caused the formation of larger voids, releasing the previously inaccessible PAHs. Therefore, it can be considered that the PAHs, which are in the biochar dried at 100 °C, are trapped in the pores of the biochar. Meanwhile, this part may desorb PAHs from the biochar due to the increase in the pore size of the biochar. There are differences in the degree of PAHs removal during the drying process between each biochar, which may be caused by the difference in the binding strength and interaction type between PAHs and biochar. The difference can be confirmed and observed through the characterization of various features, such as the specific surface area of biochar and the existence of different adsorption properties, as well as different types of adsorption sites. Thermal treatment may increase the pore diameter and specific surface area of biochar, and accelerate the volatilization of some PAHs. Because the thermal treatment method is operationally easy, cost-effective, and relatively mature, it is an economical and effective treatment strategy. It is not yet clear whether the removal process of PAHs in biochar causes secondary pollution, thus monitoring the fate of PAHs during this process is necessary.

6.2. Post-pyrolysis air oxidation

Biochar is heated in a muffle furnace containing a certain amount of air, which is called post-pyrolysis air oxidation (PPAO) (Yang et al., 2021). Under the optimized temperature and time parameters, the potential risk of biochar-derived PAHs was reduced by PPAO treatment. The oxidation of PAHs mainly occurs in the gas phase and solid phase, and the pore size of biochar increases during pyrolysis and oxidation. The free radicals produced during biomass pyrolysis and the substances carried in the pores of biochar also lead to the oxidation of PAHs and the diffusion and exchange of O_2, reactive oxygen species, and PAHs molecules. In addition, oxidation can also be carried out by heating the biochar itself to raise the local temperature, reducing the formation of PAHs (Yang et al., 2021). Therefore, the decrease of PAHs in biochar prepared by this method is attributed to the mechanism of pore filling. However, its bioavailability, adsorption performance, and toxicity need to be further studied. PPAO is an effective method to reduce PAHs in biochar due to its versatile features of low economic cost, and better degradation effect, which has a high probability of being widely used in the future.

6.3. Chemical modification

There are several ways to chemically modify and control biochar-associated PAHs, such as introducing oxidants, ultraviolet irradiation (sunlight), co-pyrolysis between biomass and heteroatom doping (Hung et al., 2022; Khalid and Klarup, 2015). This section would summarize the effects, advantages, and disadvantages of these methods.

Chemical modification is mainly done by introducing oxidants (such as hydroxyl radicals) into the biochar during the photooxidation process (Ahmed et al., 2014; Vela et al., 2012; Venny et al., 2014). Some studies have also used chemical oxidation to reduce PAHs in biochar (Khalid and Klarup, 2015). For example, Khalid and Klarup (2015) used oxidizing agents $Na_2S_2O_8$ and H_2O_2 to oxidize sawdust biochar for 4 days. At the same time, the biochar made from sawdust and sugar cane was exposed to sunlight for 8 days outdoors, and water was added in time. The chemical oxidation of wood biochar and a gasified wood/-*Arundo donax* mixture resulted in decreases in its 6-ring PAHs, but overall significant increases in PAHs concentration total for both biochar. Some 3-ring and 4-ring PAHs concentrations increased, but the total PAHs concentration decreased when the mixture-derived biochar was exposed to sunlight. It shows that exposing biochar to sunlight and rain before application helps to reduce the potential pollution of biochar to soil (Khalid and Klarup, 2015). Other research has found that washing biochar with water rich in hydrophobic organic pollutants (such as natural lake water) can reduce the content of PAHs in biochar (Chen et al., 2019). PAHs inherently formed from pyrolysis can be released accompanied with the leaching of hydrophobic organic compounds and metals (Chen et al., 2019). Therefore, the direct sunlight with water treatment in the chemical modification method has a better degradation effect. Nevertheless, whether the biochar modified by these chemical methods can reduce its toxicity is not yet known, so further research investigation is needed. In addition, a recent study also reported that PAHs degrading bacteria could be loaded on biochar for the sake of degrading PAHs and reducing environmental pollution hazards (Yza et al., 2021).

Several studies have attempted to reduce the content of PAHs in biochar by utilizing multiple biomass or biomass co-pyrolysis with iron salts. Research showed that the effects of suppressing PAHs varied. For example, the PAHs profile was improved by combining willow and sewage sludge and using CO_2 as a carrier gas. The percentage of 3–6 rings PAHs in biochar prepared with willow and/or CO_2 atmosphere is lower than that of sewage sludge biochar prepared only under an N_2 atmosphere (9.00%–62.80%) (Konczak et al., 2019). The co-pyrolysis of various biomass can promote the growth of roots of *Lepidium sativum*, reduce the mortality of *Candida* as well as the toxicity of sludge biochar (Konczak et al., 2020). Biochar prepared by the co-pyrolysis of barley straw with iron salts ($FeCl_3$ or $Fe(NO_3)_3$) showed a 21.00%–33.00% reduction in PAHs formation compared to barley straw alone, especially at 500–650 °C. This inhibition varied for different PAHs compounds, as $FeCl_3$ reduced the formation of naphthalene and acenaphthylene, whereas fluorene and phenanthrene remained unchanged. The loading of $Fe(NO_3)_3$ accelerated the generation of a large amount of naphthalene while inhibiting the formation of other PAHs molecules. The suppressed PAHs formations were due to the generation of more reduced state iron, such as Fe and FeO, in the anoxic pyrolysis atmosphere, which reduced two important PAHs precursors, C_2H_2 and C_6H_5OH. Although iron loading on biomass during pyrolysis reduced PAHs content in biochar, it increased the accumulation and toxic equivalent values of HMW-PAHs in biochar (Zhao et al., 2020).

In the preparation of biochar, heteroatom doping can inhibit the formation of PAHs. The results showed that doping different atoms (N, B, O, NB, and NS) in biomass could reduce the content of PAHs in wood biochar by 85.00%–97.00% (Hung et al., 2022). In addition, the content of PAHs in pineapple leaves and distillers grains biochar doped with different heteroatoms (N, B, O, P, NB, and NS) decreased by 49.00%–96.00% and 18.00%–97.00%, respectively (Hung et al., 2023a, 2023b). Among them, B doping significantly reduced the content of PAHs in biochar from distillers grains (97.00%), and NS significantly reduced the content of PAHs in biochar from pineapple leaves (96.00%). B doping can destroy the sp^2 hybrid carbon in biochar, thus inhibiting the formation of PAHs (Pan et al., 2023). NS doping can inhibit the formation of PAHs by oxidizing PAHs precursors. Due to the simultaneous introduction of N and S atoms, the high electronegativity of S can induce the polarization of adjacent N or C atoms, thus overcoming the chemical inertia of the C network and changing the electron distribution in biochar (Dong et al., 2023). Overall, heteroatom doping can regulate the electronic distribution of biochar and effectively inhibit its PAHs formation. Therefore, heteroatom doping is a strategy to prepare high-quality biochar and reduce ecological risk, but its doping cost and mechanism need to be studied.

The changes in PAHs composition in different modified biochars were different, and their treatment results were inconsistent. Different treatment methods cause the content of some PAHs to increase or decrease in biochar (Fig. 6), but the overall total content of PAHs in biochar decreases. The PAHs reduced by chemical modification are mainly LMW-PAHs, and only water washing and sunlight exposure are used to remove HMW-PAHs as demonstrated in Fig. 7. Pretreatment of biochar with water washing or sunlight irradiation before biochar application can effectively reduce the potential hazard of biochar. Co-pyrolysis biomass can effectively inhibit the formation of PAHs in biochar, especially regarding the significant inhibition effect of metal-free doping (N, S, B, and NS) on the formation of PAHs in biochar. However, most of them use chemical modifiers for co-pyrolysis to reduce PAHs in biochar, and there is relatively little research on co-pyrolysis of low-cost waste.

6.4. Other methods

It has been suggested that the carrier gas significantly affects PAHs content in biochar. The carrier gas can alter the secondary reaction by changing the vapor to the solid contact time, thus limiting the formation and recondensation of PAHs during pyrolysis (Buss et al., 2016). A previous study confirmed that biochar with low PAHs concentration can be obtained at higher carrier gas flow rates (Madej et al., 2016). Higher N_2 flux reduces the chance of condensation of aromatic groups, which promotes the conduction of PAHs precursors in the gas flux, thereby inhibiting PAHs formation (Buss et al., 2016). In addition, the change from N_2 to CO_2 can reduce the total content of PAHs in sludge biochar, while carbon radicals can change the distribution of PAHs. Meanwhile, it positively increased the ratio of light compounds in biochar (Konczak et al., 2019). Biochar produced at CO_2 ambient had fewer negative effects on jump worms than biochar pyrolyzed in N_2 (Konczak et al., 2020). Therefore, CO_2 may serve as the optimal carrier gas for pyrolysis medium and establish an environmentally friendly and energy-saving process in the future.

Moreover, the artificial aging and field aging of biochar reduced its PAHs content (Krzyszczak et al., 2022b; Oleszczuk and Koltowski, 2018), indicating that PAHs in biochar were desorbed and released. Oleszczuk and Koltowski (2018) studied the total PAHs, freely soluble PAHs, and changes in toxicity of biochar treated by different aging processes (chemical, biological, and physical aging). They found that both the content of PAHs and toxicity were reduced, which was a positive tendency. Biochar has different effects on animals and plants after aging (Liu and Fan, 2022). Aged elephant grass biochar increased the mortality of *F. candida* and reduced the negative impact on the growth of the *L. sativum* roots (Oleszczuk and Koltowski, 2018). Research has shown that biochar aging may reduce biochar toxicity, which was similar to the findings of Sigmund et al. (2017). Therefore, aging is an effective way to reduce PAHs and their toxicity in biochar.

In addition to focusing on mitigation strategies for PAHs in biochar, the ultimate fate of PAHs during processes of water washing, heat treatment, post-pyrolysis air oxidation, and aging should be concerned (Fig. 8). As shown in the figure, the fate of PAHs may lie in the residual PAHs in the gas phase, water phase, and biochar. In summary, most methods for degrading PAHs in biochar mainly remove some PAHs, which are volatile and easily soluble in water. The good degradation strategies are thermal treatment and water washing. Thermal treatment can effectively remove PAHs from biochar, while water washing can also remove ash and some heavy metals. However, the combination of heat treatment and water washing and other potential parameters optimization (pyrolysis temperature) to obtain safe biochar requires further research.

7. Conclusions and future perspectives

This review summarizes the characteristics of PAHs in biochar, their formation mechanisms, possible toxicity concerns, potential mitigation strategies as well as possible ways for the safe usage of biochar for environmental applications. The content of PAHs in biochar is mainly affected by temperature and feedstocks. The content of PAHs in most biochar prepared at 500–600 °C was higher than those at other temperatures. The PAHs content in biochar exhibited an order of green waste biochar>agricultural waste biochar>poultry manure biochar>woody waste biochar>industrial waste biochar>food waste biochar. When biochar is used in the environment, it is recommended to use a combination of health assessment, toxicity equivalent value, and ecotoxicological methods to evaluate the risk associated with PAHs. The thermal treatment method has been demonstrated as the best control effect of PAHs in biochar, followed by biomass co-pyrolysis, water washing, and sunlight irradiation routes. The mitigation strategies can effectively reduce the concentration of PAHs in biochar, thus reducing its toxicity and making it safe and widely applicable. Therefore, research on more new mitigation strategies of PAHs in biochar would be the development trend in the future.

At present, plenty of methods are available to reduce PAHs in biochar, but still, biochar is facing some challenges and difficulties for environmental remediation and soil improvement purposes after treatment. The future research directions to be considered are as follows:

Firstly, although IBI and EBC stipulate the threshold of the total content of PAHs in biochar respectively, it is still necessary to establish the risk assessment model and reference-quality value of PAHs in biochar. To further evaluate the risk level of biochar, it is necessary to determine the application amount and feasibility of biochar in different environments, as well as how biochar can reduce PAHs during the application process. PAHs in biochar have different effects on different organisms and plants. The fate of PAHs in water or soil is also affected by many factors, especially the degradation and bioavailability of PAHs in soil and the accumulation in plants are more complex. Therefore, before the large-scale application of biochar, it is necessary to carry out long-term and a large number of experiments to evaluate its risk and formulate more specific standards (risk assessment model and reference-quality value).

Secondly, in addition to the common acetylene dehydrogenation and joint action of hydrogen abstraction, other formation mechanisms of PAHs further need to be understood. Feedstocks and pyrolysis temperature are the main factors affecting the formation of PAHs in biochar. Therefore, it is necessary to further study the impact of biomass interaction on the formation of PAHs and reveal how pyrolysis temperature affects the content of PAHs in biochar, which helps understand the formation mechanisms of PAHs.

Thirdly, the mechanisms of how these mitigation strategies remove PAHs from biochar and their adsorption properties after removal are still not clear. It is helpful to determine the environmental application potential of biochar after treatment. Modified biochar (metal biochar and biochar doped with heteroatoms) minimized the content of PAHs in biochar. However, the relationship between the biochar prepared with different loading ratios and the content of PAHs in the biochar is still lacking. Finding a suitable modification method that reduces the content of PAHs in biochar while improving its adsorption efficiency is an important research direction in the future. Moreover, the distribution and whereabouts of PAHs in biochar treatment are not clear. It may cause secondary pollution to the environment if released into the atmosphere. Therefore, it is necessary to explore the fate of PAHs and develop mitigation strategies that have no secondary pollution to the environment. Among them, the method of loading PAHs degrading bacteria on biochar is worth exploring to control PAHs related to biochar. Thus, the exploration of eco-friendly mitigation strategies is the future research direction.

Finally, future research should focus on developing precise quantitative evaluation techniques and monitoring strategies for PAHs linked with biochar, such as Nuclear Magnetic Resonance and Fourier Transform Ion cyclotron Resonance Mass Spectrometry. Moreover, the

mechanisms of how PAHs are retained in or released from biochar also need to be clarified under a variety of soil and climatic circumstances.

CRediT authorship contribution statement

Canxu Yao: Writing – original draft, Investigation, Formal analysis. **Bing Wang:** Writing – review & editing, Formal analysis, Conceptualization. **Jian Zhang:** Writing – review & editing. **Muhammad Faheem:** Writing – review & editing. **Qianwei Feng:** Writing – review & editing. **Masud Hassan:** Writing – review & editing. **Xueyang Zhang:** Writing – review & editing. **Xinqing Lee:** Writing – review & editing. **Shengsen Wang:** Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

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