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Biochar aging: Mechanisms, physico-chemical changes, assessment, and implications for field applications

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ABSTRACT

Biochar has triggered a black gold rush in environmental studies as a carbon-rich material with well-developed porous structure and tunable functionality. While much attention has been placed on its apparent ability to store carbon in the ground, immobilize soil pollutants, and improve soil fertility, its temporally evolving *in situ* performance in these roles must not be overlooked. After field application, various environmental factors, such as temperature variations, precipitation events and microbial activities, can lead to its fragmentation, dissolution and oxidation, thus causing drastic changes to the physico-chemical properties. Direct monitoring of biochar-amended soils can provide good evidence of its temporal evolution, but this requires long-term field trials. Various artificial aging methods, such as chemical oxidation, wet-dry cycling and mineral modification, have therefore been designed to mimic natural aging mechanisms. Here we evaluate the science of biochar aging, critically summarize aging-induced changes to biochar properties, and offer a state-of-the-art for artificial aging simulation approaches. In addition, the implications of biochar aging are also considered regarding its potential development and deployment as a soil amendment. We suggest that for improved simulation and prediction, artificial aging methods must shift from qualitative to quantitative approaches. Furthermore, artificial pre-aging may serve to synthesize engineered biochars for green and sustainable environmental applications.

KEYWORDS: soil carbon; remediation; heavy metals; soil health; climate change mitigation

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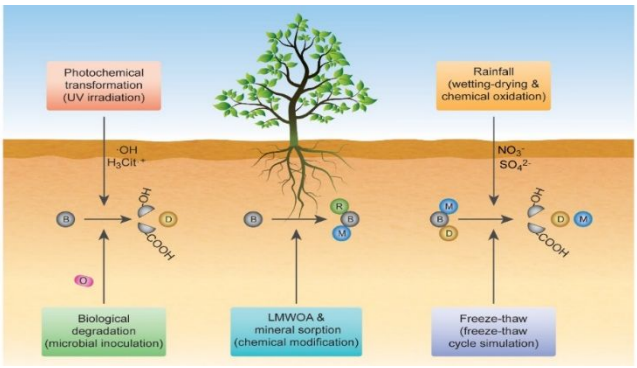
40 

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1 INTRODUCTION

Biochar is a carbon-rich porous material that is produced by the pyrolysis or hydrothermal carbonization of raw biomass [1, 2]. While new applications for biochar continue to emerge (e.g., as a catalyst), in general, uses for this material have divided in two directions. One is as an alternative to activated carbon usage in wastewater [3-5] or flue gas treatments [6]. The other is as a soil amendment. Biochar's promise as a soil amendment is tremendous because it offers multiple functions, including increased soil fertility [7, 8], the remediation of polluted soils [9, 10], and *in situ* carbon sequestration as a way to mitigate climate change [11].

Land degradation issues around the world hinder global efforts toward meeting food demand [12-15]. Since the discovery of *Terra Preta de índio*, an anthropogenic black and extremely fertile soil in Amazon Basin enriched with charcoal (biochar) [16, 17], there seems to be a "black gold rush" over the past few decades. Today, biochar again promises a potential route to sustainable food security owing to its ability to increase soil fertility levels in various ways including the provision of labile organic carbon, improved soil nutrient retention, improved soil structure, improved water holding capacity, neutralized soil acidification, and more amenable growing conditions [16, 17]. Meta-analysis of 371 plant productivity studies in soils amended with biochar has indicated its ability to significantly increase aboveground productivity and crop yields ($p<0.01$ for both productivity and yield, increase by 30% and 19% on average, respectively) [18].

Meanwhile, the industrialization of developing countries has resulted in heavy metal(loid) contamination across large areas of agricultural land. In China, for example, analysis of 1041 soil samples throughout the country reveals that cadmium is widely encountered in agricultural soils (0.01 – 74.75 mg/kg, with the average value of 0.87 mg/kg), leading to concerns over rice crops being

64 contaminated and unsafe for consumption [19, 20]. Over 3.3 millions of hectares of agricultural land are
65 now too contaminated to use due to such pollution issues [21]. Biochar's capability to immobilize
66 harmful soil contaminants *in situ* suggests that this material also promises a potential route to improve
67 food security in areas affected by contaminated soils [9, 22-24].

68 Furthermore, soils are a major factor for global greenhouse gas (GHG) emissions and must feature
69 in efforts to tackle the climate crisis. Because biochar's carbon structure is known to be recalcitrant
70 within the soil environment, biochar production and field application offers a potential route to
71 removing carbon from the atmosphere (i.e., during biomass growth) and long-term storage. It is
72 estimated that production of biochar and its field application could potentially offset 12% of
73 anthropogenic CO_2-C equivalent emissions (i.e., 1.8 Pg CO_2 *vs* 15.4 Pg CO_2 per year) [11].

74 Although the number of biochar-related studies are booming, the long-term environmental
75 behaviors of biochar are much less explored compared with other research areas such as short-term
76 remediation performances. Once applied to the soil, biochar undergoes an aging process. Various
77 natural forces, such as freeze-thaw cycles (induced by variations in temperature) [25], wetting-drying
78 cycles (caused by rainfall events) [26], photochemical degradation (as a result of sunlight irradiation) [27]
79 and mild oxidation (caused by atmospheric oxygen, root exudates or microorganisms) [28, 29] lead to
80 significant changes in biochar physicochemical properties, such as the specific surface area (SSA),
81 surface morphology, acidity, elemental composition, ion exchange capacity and the aromaticity. Such
82 changes could either be to the enhancement or detriment of biochar's performance for field
83 applications and long-term carbon storage over time. However, the long-term behavior of biochar
84 within the soil environment has not yet been summarized in sufficient detail. It is time-consuming to
85 monitor the long-term effects of biochar application, since some of the natural aging process can be
86 very slow (half-life more than 1000 years) [30]. Therefore, various artificial aging methods, such as

chemical oxidation, physical aging and the biological aging have been proposed as proxies for natural aging, cutting the aging duration from years or months to days or hours.

Based on various aging mechanisms, changes in biochar properties could either enhance or inhibit biochar's performances in soil amendment, environmental remediation and climate change mitigation. Furthermore, to embrace a healthy and sustainable agroecosystem, it is necessary to comprehend the role of long-term biochar field application in both agricultural and remediation aspects. The aims of this review are to 1) propose biochar aging mechanisms, and examine aging-induced changes in biochar physico-chemical properties; 2) explore the effects of biochar aging on the basis of aging-induced changes in biochar properties; and 3) comprehend the role of biochar long-term aging in sustainable agriculture using a generalized framework. Challenges and potential future research directions are also put forward.

2 MECHANISMS

Biochar in the soil is subject to various natural aging mechanisms. As biochar's carbon content is largely recalcitrant, full mineralization (e.g., biochar conversion to H_2O and CO_2), either by biotic or abiotic pathways is slow, with reported half-lives in the order of 1000 years [30]. Aging mechanisms that result in changed properties are relatively quicker, yet these are still slow to observe in the field. Artificial accelerated aging methods, which mimic natural aging mechanisms, can significantly reduce observation times. The most relevant biochar aging mechanisms are illustrated in **Figure 1** along with implications for artificial accelerated aging methods.

Biochar aging can occur from natural rainfall or freeze-thaw events in seasonally frozen areas which leads to mechanical fragmentation, surface oxidation, dissolved organic matter (DOM) release and

mineral dissolution (i.e., decreased ash content). Such environmental processes can be accelerated experimentally by wet-dry cycling, chemical oxidation and freeze-thaw cycling. Soil mineral interaction with biochar can result in pore blockage and increased biochar mineral content, whereas biochar adsorption of root exudates may cause acidification and mineral dissolution. These processes can be accelerated experimentally by chemical modification. Biological and photochemical processes can result in oxidation and release of biochar's labile carbon content, which can be accelerated experimentally by microbial inoculation and UV irradiation, respectively. The specific mechanisms involved in biochar aging are discussed in the subsections below.

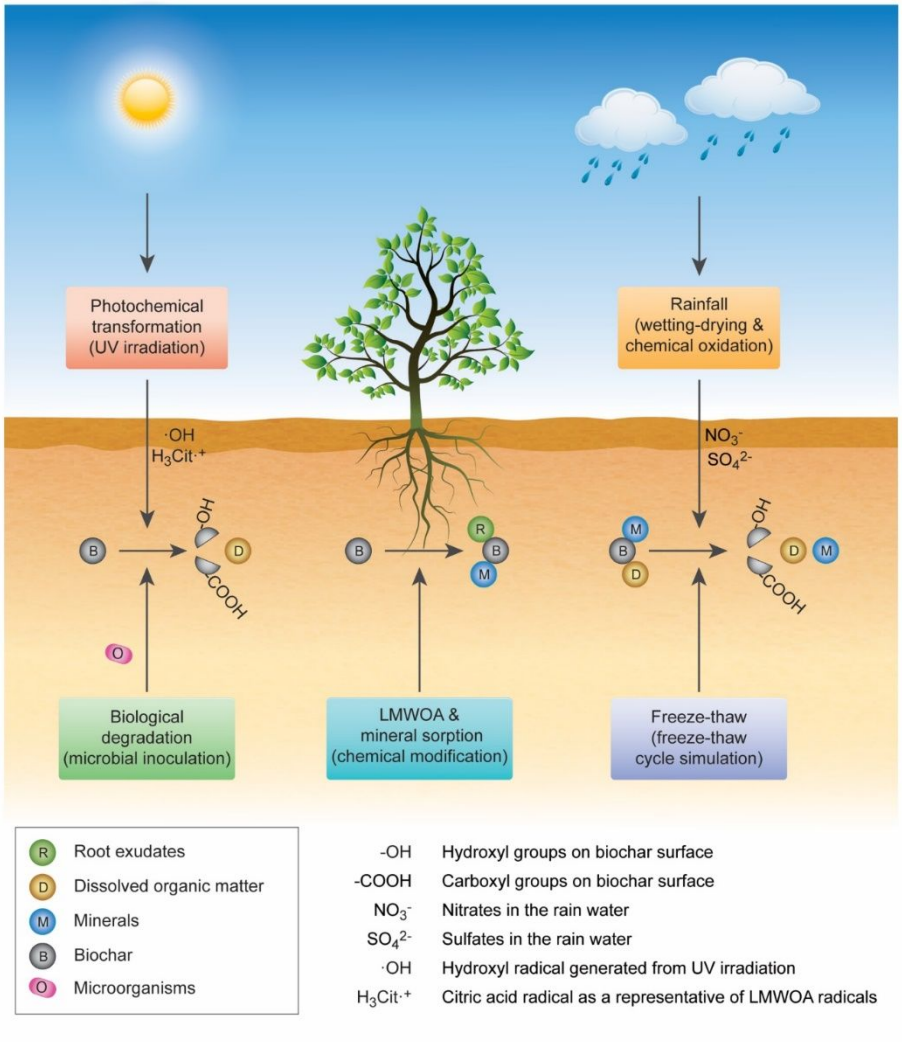


Figure 1. Biochar field aging mechanisms and implications for artificial accelerated aging shown in parenthesis.

2.1 Dissolution

The dissolution of mineral components (de-ashing) is an important aging process with agronomic implications. Mineral dissolution from biochar can be divided into two stages [31]:

Stage 1 – Initial rapid element detachment induced by ion exchange, submicrometer particle dissolution, and preferential dissolution at crystal imperfections (last for t_1 h);

Stage 2 – pH-dependent zero-order reaction (Eq. 1) [31]:

$$R_i = K_i[\mathrm{H}^+]^n \quad (1)$$

where R_i is the zero-order (constant) reaction rate of element *i* (e.g., K, Ca, Mg, P), K_i refers to mineral specific rate constant of element *i*, $[\mathrm{H}^+]$ represents the proton activity, *n* is the reaction order for $[\mathrm{H}^+]$.

Therefore, the total amount of elements released can be calculated as follows (Eq. 2):

$$Q_{it} = Q_{i1} + R_i(t - t_1) \quad (2)$$

where Q_{it} represents the total amount of released element *i* after these two stages, Q_{i1} refers to the amount of element *i* during the first stage, *t* is the reaction time.

The dissolution kinetics for different elements may vary. The first stage dissolution of Ca, Mg and P could last for 24 h, releasing substantial amount of elements from corn straw biochar (27%, 47%, 41% of the total Ca, Mg and P content, respectively). After that, the pH-dependent dissolution of Ca

($R_{Ca} = 0.049$ at pH 6.9) and Mg ($R_{Mg} = 0.108$ at pH 6.9) could be faster as compared with P ($R_{Mg} = 0.016$ at pH 6.9) [31]. Nevertheless, the element K does not obey this two-stage rule, which could be released very rapidly (i.e., release 30% at the first hour in aqueous solution) [31]. A study by Limwikran et al. [32] even observed that the large amount of K released from the fruit waste biochars (i.e., 16,201 – 33,843 mg/kg) could have displaced sufficient exchangeable Ca from the soil, thus increasing the total Ca in biochar (i.e., by 2,144 – 11,098 mg/kg) after incubation for 8 weeks in different tropical soils.

Various natural or anthropogenic events will lower soil pH levels (e.g., the introduction of H^+), leading to greater mineral release from biochar (**Figure 1)**. Rainfall events are the most important contributor of soil acid. Typically, rainwater is slightly acidic (pH ~ 5.6) due to dissolved CO_2 (i.e., carbonic acid). In the case of acid rain, dissolved air pollutants, such as NO_X and SO_2, results in much a lower pH value (pH ~ 4) and greater levels of H^+ being introduced to soils [33]. Moreover, plants release low molecular weight organic acids (LMWOAs), such as citric acid, malic acid, oxalic acid, acetic acid or formic acid, which can also cause biochar minerals to dissolve in the rhizosphere [28, 34, 35]. This rhizosphere effect has been reviewed in-depth elsewhere [35, 36].

2.2 Fragmentation

Mechanical disintegration is an important, yet often overlooked, aging mechanism. Rainfall and freeze-thaw cycles are the dominant causes of biochar physical fragmentation and breakdown in the field (**Figure 1)**. During rainfall events, water sorbed in biochar can cause graphite sheets to swell, resulting in structural expansion (**Figure S1**) [37]. Expansion and shrinkage of water molecules during the freeze-thaw cycles can also cause physical fragmentation [38]. Compared with more flexible raw biomass, biochar will tend to fracture at relatively low strain under mechanical stress. These structural

158 defects lead to fragmentation (**Figure S1**) [37, 39]. Small biochar particles can form in this way, which
159 are termed dissolved black carbon, with no detectable change to the elemental composition or other
160 chemical properties [37].

161 **2.3 Interactions with soil minerals**

162 After biochar is applied to the soil, minerals can interact with it through adsorption reactions and
163 attach onto the biochar surface (**Figure 1**). The adsorption of soil minerals onto biochar can shield it
164 from decomposition and oxidation processes, and the formation of biochar-mineral complexes
165 enhances long-term carbon sequestration [40, 41]. Soil minerals, such as kaolinite, montmorillonite, iron
166 oxides and aluminum oxides can attach tightly to biochar surfaces through the formation of surface
167 complexes such as Fe-O-C, or by incorporation into inner pores, resulting in pore clogging [42] and
168 enhanced oxidation resistance [43]. A relatively high Al concentration has been observed at the interface
169 between soil minerals and aged biochars, suggesting the vital role of Al-containing minerals in this
170 interaction [40]. Kaolinite could enhance the oxidation resistance of walnut shell biochar, since the
171 content of oxygen-containing functional groups for kaolinite protected biochar was much lower than
172 that of biochar exposed to air after 3 months incubation (16.1% vs 36.3%) [43]. It could be that the soil
173 minerals protected the biochar surface from oxidation via forming a physical barrier (**Figure 2e**).
174 However, we found that most studies have overlooked the role of soil mineral interactions in assessing
175 biochar aging.

176 **2.4 Biological degradation**

177 The well-developed porous structure of biochar offers a significant microbial habitat niche [44, 45]. It
178 has long been established that extensive colonization occurs for biochars subjected to hundreds of
179 years of natural aging [46, 47], yet it is still debated whether soil organisms will colonize biochars

effectively in a relatively short aging duration (i.e., several years). After 3 years of field aging, the wood biochar remained sparsely colonized due to the lack of labile carbon [48]. In comparison, grass biochars can not only be easily colonized, but also used as a substrate only after 90 days of short incubation [49]. It is therefore proposed that the carbon bioavailability determines the speed of microbial colonization. The higher the labile carbon content (e.g., aliphatic C compounds), the more rapid the colonization [45]. In addition, the physical fragmentation (i.e., the exposure of more interior surfaces) and abiotic oxidation (i.e., the disintegration and partial oxidation of recalcitrant C) may have accelerated the colonization process [48].

Complete mineralization of biochar (to H_2O and CO_2) by microorganisms may take hundreds to thousands of years [30, 50], whereas changes in biochar properties may also be significant due to microbial colonization and degradation after several years of field application. Soil microorganisms play an important role in biochar surface oxidation and labile carbon loss owing to the introduction of additional oxygen-containing functional groups and DOM release (**Figure 1**) [51]. At the initial stage of microbial degradation, the breakdown of aliphatic C compounds results in the disconnection of aromatic moieties and oxidation at the break points [52]. After mineralization of labile C pool in the short term (usually between 2 to 60 days) [53], the degradation rate of biochar carbon decreases dramatically. A ^{14}C isotopic labelling study suggested that the decomposition rate of ryegrass biochar could be very high (up to 0.15% d^{-1}) during the first two months of incubation. After that, the decomposition rate decreased sharply to 0.0015% d^{-1} and remained stable [50]. Fungi are known to degrade recalcitrant carbon in soil [54, 55]. An increase in fungal biomass during the second stage of biochar degradation indicated that fungi played vital roles in microbial decomposition of recalcitrant aromatic moieties [54]. In particular, saprophytic fungi (e.g., white-rot fungi) could break down highly

condensed aromatic structures such as lignin [56, 57] and polycyclic aromatic hydrocarbons (PAHs) [58, 59], accounting for the long-term degradation of biochar in soil [60].

Soil fauna also contribute to the biological degradation of biochar [53]. As the most widely explored soil macroorganism, earthworm accelerates the aging process via different pathways. Firstly, soil bioturbation and ingestion of biochar by earthworms results in the physical disintegration, thus favoring the abiotic or microbial decomposition [53]. In addition, biochar can be inoculated with microorganisms (e.g., Firmicutes, Actinobacteria, Proteobacteria) while passing through the guts [61-63]. Considering that microbial colonization could be a slow process for biochars with a high recalcitrant C content (i.e., aromatic rings) [48], the earthworm-facilitated microbial inoculation may have accelerated the microbial aging. Very limited data suggest that other soil macroorganisms, such as nematodes and arthropods may also be involved in biochar aging. Application of wheat straw biochar significantly increased the abundance of fungivore nematodes (p<0.05), which may in turn regulate biochar degradation via alterations in soil fungal community [64]. Fecal pellets from arthropods have been observed within a charcoal-rich layer of the forest soil, suggesting that biochar can be ingested and processed by these animals [65, 66]. There is an urgent need to explore the role of these macroorganisms in long-term biochar degradation.

2.5 Abiotic oxidation

Biochar oxidation can occur abiotically or biotically, with a number of studies suggesting that abiotic oxidation plays the dominant role [67-71]. Abiotic biochar oxidation has been observed to occur through various processes.

Atmospheric oxygen-induced oxidation can introduce additional oxygen-containing functional groups, such as hydroxyl, carbonyl and carboxyl, to the biochar surface. This mild oxidation process

is slow at ambient temperature [72]. For instance, atmospheric aging of sludge biochar for 2 months could only increase the amount of oxygen-containing functional groups by 2% (incubation temperature 45 °C, measured by the Boehm titration method) [72]. Rainfall events can also result in biochar oxidation owing to the dissolved oxygen and nitrogen oxides in rainwater [73-75]. Rainfall events can also lead to physical disintegration and acidification, thus causing labile carbon to be released as DOM, minerals to leach out and additional oxygen-containing functional groups, such as hydroxyl, carbonyl and carboxyl, to be introduced to the biochar surface. It is not yet clear whether biochar is oxidized during freeze-thaw processes. Some studies have reported slight increases in the surface oxygen content, although the precise oxidizing mechanism is unknown [38, 76]. Others studies did not observe any significant changes to biochar's elemental compositions after freeze-thaw cycles [77].

Photochemical transformation has been observed to be a key abiotic oxidation mechanism. The dissolved black carbon released from biochar could generate reactive oxygen species (ROS), including the hydroxyl radical (·OH), singlet oxygen ($^1O_2$), and superoxide (O_2^-) (i.e., the self-generation of ROS) [27, 78], which will in turn lead to the phototransformation of biochar. For instance, the dissolved organic carbon from the bamboo biochar could generate $^1O_2$ more effectively (apparent quantum yield 4.07%) than many well-studied photoactive components in terms of ROS generation (apparent quantum yield fell within 1.18% - 2.48%) [79]. In addition, ROS can also be generated directly from the biochar matrix. For instance, the carbon matrix of crop residue biochars generated 10% - 45% $^1O_2$ and 64% - 75% ·OH, whereas the dissolved organic matter derived from biochars accounted for 47% - 86% $^1O_2$ and only 4% - 12% ·OH generation [80]. Fenton-like reactions, either with the presence of LMWOAs (**Section 4.2.2**) [27] or persistent free radicals (PFRs) [80], favor the formation of the ·OH.

Aromatic ketones [81], aromatic amino acids [82] and quinones [80] are potential chromophores for $^1O_2$, whereas the silica minerals [79] and the phenolic groups [83] in biochar play vital roles in O_2^- generation.

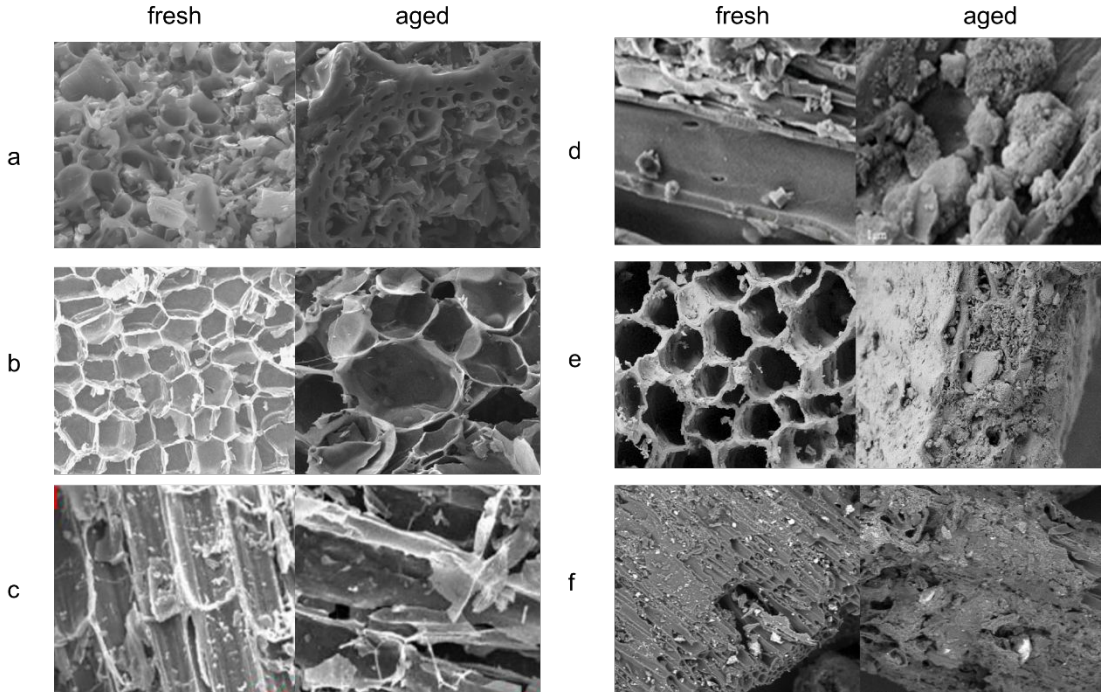
3 PHYSICO-CHEMICAL CHANGES

Biochar will display a series of physical and chemical changes overtime due to being subjected to aging processes. These physico-chemical changes are discussed in the sub-sections below.

3.1 Physical changes

Compared with fresh biochar, both naturally aged and artificially aged biochars can display significant differences in their surface morphologies, as revealed by scanning electron microscopy (SEM) imaging (**Figure 2**). The blockage or fragmentation of the biochar structure will affect properties such as the surface area, pore volume and the pore diameter. It has been reported that 3 years of natural field aging in the Qinghai Tibetan Plateau caused the surface morphology of rice husk biochar to become much rougher and show signs of collapse (**Figure 2a**) [84]. Even when biochar is not applied to soil, atmospheric oxidation can lead to much more irregular structures (**Figure 2b**) [85]. Compared with natural aging, the effects of artificial aging on biochar surface morphologies tend to be more pronounced. For example, biochar subjected to artificial wet-dry cycles revealed ruptured pores (**Figure 2c**) [38]. Artificial chemical oxidation can lead to the presence of floccules of oxidized matter on biochar surfaces [74] (**Figure 2d**). SEM images have revealed that biochar interactions with fine clay particles can lead to severe pore blocking (**Figure 2e**) [42]. Biological aging can also lead to the blocked pores due to microbial coating (**Figure 2f**) [86]. Substantial changes in surface morphology is closely related to the environmental implications (**Table S2**). The exposure of more interior surfaces due to pore collapse results in enhanced exposure and dissolution of inorganic minerals, thus

267 promoting plant growth in the long run [84]. Although aging with soil minerals will block the pores, the
268 adsorption capacity towards contaminants could be increased due to the high surface area of the
269 attached minerals (**Table S2**) [42].



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271 **Figure 2.** Scanning electron microscopy (SEM) images revealing the surface morphology of fresh
272 and aged biochars subjected to various aging methods. (a) Rice husk biochar, naturally aged for 3
273 years in the field [84]. (b) Pine wood biochar formed during a wildfire event, naturally aged outdoors
274 for 10 years without any contact with soil [85]. (c) Corn stalk biochar, physically aged through artificial
275 wet-dry cycles [38]. (d) Rice straw biochar, artificially aged through HNO_3/H_2SO_4 oxidation [74]. (e) Pig
276 manure biochar, chemically aged by interaction with soil minerals [42]. (f) Biosolid and green waste co-
277 pyrolyzed biochar, biologically aged through composting [86]. All images are reproduced with
278 permission.

The specific surface area (SSA) of biochars can either increase or decrease because of aging. Usually, the SSA_{aged}:SSA_{fresh} ratio will fall between 0.5:1 and 2:1 (**Figure 3a**). A few studies have reported more extreme changes. One study of natural biochar aging reported a 4.5:1 ratio, which was attributed to large amounts of labile carbon loss [87]. Another study involving artificial chemical oxidation induced aging reported a 0.09:1 ratio, which was attributed to the collapse of inner pores [88].

Aging-induced changes to biochar surface area are usually related to biochar oxidation, mineral dissolution, DOM release, or sorption processes that affect the biochar pore structure. For example, increased SSA values after aging may stem from the formation of new pores by the aggregation of biochar and biochar-derived organic substances [38], dissolution of labile carbon [89], or chemical oxidation of biochar carbon compounds in acidic or alkaline conditions [71]. In contrast, several mechanisms are attributed to decreased SSA values after aging, including the blockage of pore structures due to the dissolution-precipitation of inorganic minerals [38], the formation of oxygen-containing functional groups at pore entrances [88], or physical clogging by soil substances [90].

According to the literature reviewed, the total pore volume (TPV) may either increase or decrease (TPV_{aged}: TPV_{fresh} fell between 0.01:1 and 3.33:1) due to the similar mechanisms. As for pore diameter, current studies suggest that biochar aging may lead to the formation of meso- and micro-sized pores. Some studies have indicated that mesopores are more likely to form during chemical oxidation, as evidenced by N_2 adsorption isotherms changing from IUPAC Type I (fresh biochar, microporous) into Type IV (aged biochar, mesoporous) (**Figure S2**) [29, 71, 91]. Others have reported that natural aging favors the formation of micropores [89]. This finding was probably due to labile carbon being leached out or degraded by soil microorganisms. Compared with soil fertility improvement, aging-induced changes in porous structure affects more on remediation purposes. Higher surface area indicates more available sites for contaminant binding (especially for organic contaminants) [9, 22]. A

well-developed meso- and micro-pore structure enhances contaminant adsorption via pore filling [42, 92]. Therefore, an increase in specific area and pore volume favors the immobilization of soil contaminants, and vise versa (**Table S2**) (**Section 5.2**).

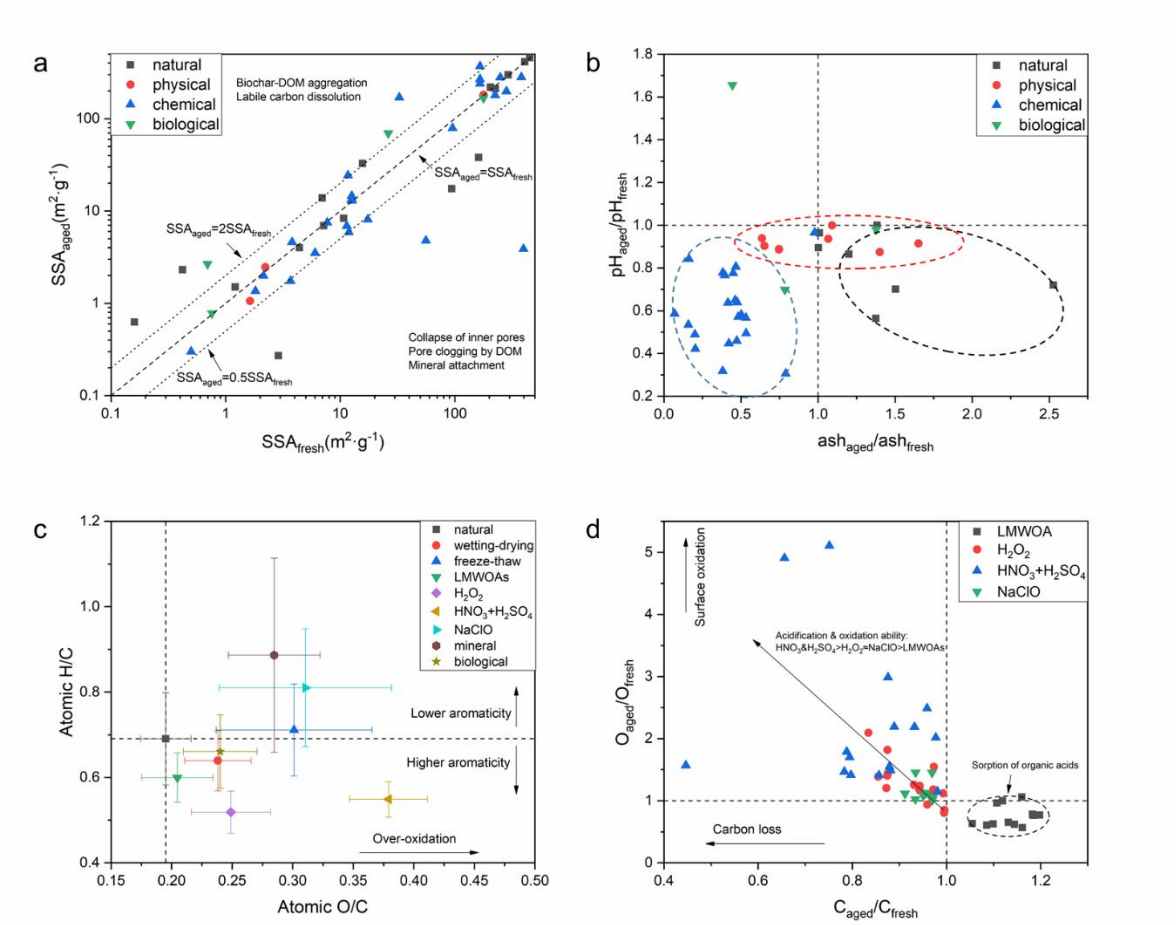


Figure 3. Reported changes to biochar chemical properties due to aging: (a) specific surface area (SSA); (b) ash content and pH; (c) van Krevelen diagram for biochars subjected to various aging processes; (d) carbon loss and surface oxidation during chemical aging. Literature values are provided in **Table S3**.

3.2 Chemical changes

Biochar aging can reduce its ash content and increase its acidity level (i.e., lower pH value). Aging by chemical oxidation results in biochar acidification and the release of ash minerals whereas physical aging is much milder, resulting in only slight variations in biochar pH. In general, the acidification effect is in the order of chemical > natural > physical (**Figure 3b**). This is because chemical aging by oxidation (using H_2O_2, HNO_3, H_2SO_4, citric acid) favors the formation of acidic functional groups (e.g., carboxylic, phenolic) on biochar surfaces [28, 93, 94]. Although wet-dry and freeze-thaw cycles can also introduce oxygen-containing functional groups, these are much weaker in the context of biochar acidification [38]. Limited evidence has shown that biological aging can increase or decrease biochar pH levels. Decreased pH levels may owe to the same reasons discussed above [77]. Increased pH levels may stem from microbial activity, with one study reporting that the pH of a hydrochar increased from a relatively low initial pH level of 4.18 to 6.92 due to microbial decomposition of organic acids [29]. The acidification effect is usually an unwanted phenomenon in field applications. The decrease in soil pH as a result of biochar acidification will be detrimental to plant growth (**Section 5.1**), and mobilize metallic cations (**Section 5.2**). Furthermore, acidification may be associated with stimulated GHG emissions (**Section 5.3**).

The ash content of biochar relates to the inorganic mineral components [24]. Natural aging in the field favors the adsorption of soil minerals onto biochar surfaces, resulting in higher ash content (i.e., $ash_{aged}/ash_{fresh} > 1$). Conversely, chemical aging can cause the dissolution of biochar minerals during oxidation (i.e., $ash_{aged}/ash_{fresh} < 1$). Physical and biological aging, such as wet-dry or freeze-thaw cycles, can either increase or decrease biochar ash contents because of alternating dissolution and precipitation processes, with the resulting ash content depending on the balance of these processes (ash_{aged}/ash_{fresh} is typically 0.64 – 1.65). It is noteworthy that while physical aging does not usually

affect biochar pH levels significantly, the ash content of physically aged biochar may vary greatly from that of fresh biochar. On the one hand, the higher ash content of naturally field aged biochars indicate the presence of more inorganic nutrients (e.g., K, Ca, Na, Mg) within the charosphere [48, 95]. On the other hand, the de-ashing effect as a result of chemical aging may weaken the co-precipitation immobilization performance towards soil metals (**Section 5.2**).

Aging significantly affects the presence of biochar surface functional groups and elemental composition. Both natural and artificial aging approaches can introduce oxygen-containing functional groups, such as hydroxyl, carbonyl and carboxyl, onto biochar surfaces. This is evidenced by Fourier Transform Infrared Spectroscopy (FT-IR) and X-ray Photoelectron Spectroscopy (XPS) observations [52, 89, 93, 96-98]. As for the elemental composition, a decrease in C content and increase in O content is typically observed as biochar ages, indicating the dissolution of labile C and the formation of O-containing functional groups [38, 51, 99].

Compared with natural aging, artificial aging approaches can lead to significantly higher O:C ratios due to over oxidation (**Figure 3c**). Common chemical oxidation aging methods involve the use of HNO_3 and H_2SO_4, which can raise the O:C ratio to as much as twice that of natural aging. Freeze-thaw cycles tend to cause greater increases to the O:C ratio than wet-dry cycles (**Figure 3c**, average O:C ratio 1:4.1 *vs* 1:3.3) due to the joint effects of physical fragmentation and the presence of temperature-tolerant microorganisms (e.g., *Chryseobacterium*, *Enterococcus*, *Pseudomonas*) which use biochar labile carbon as a C source during freeze-thaw cycles [100, 101]. These microorganisms are killed by oven drying in wet-dry cycles [102, 103]. In general, artificial aging with LMWOAs presents the closest elemental composition to that of natural aging, followed by wet-dry cycling, biological aging, and last of all, chemical oxidation.

On the one hand, chemical oxidation fails to simulate natural aging (**Figure 3c**). On the other hand, the phenomenon of over-oxidation can be used to produce engineered biochars (rich in oxygen content) (**Figure 3d**). Chemical acidification with HNO_3/H_2SO_4 is the most effective way to increase O content, whilst mild oxidation with root exudates (LMWOAs) has little effect on biochar oxidation (**Figure 3d**). Biochar oxidation is usually accompanied by carbon loss due to mineralization (oxidize to CO_2) (**Figure 3d**), but LMWOAs modification will not decrease C content (due to sorption of organic acids on biochar surface). To synthesize engineered biochars, it is suggested that 1) LMOWAs-induced aging can improve soil fertility, since the organic acids act as labile carbon forms that can be easily used by plants and rhizosphere microorganisms; 2) harsh oxidant-modified biochars can be used for contaminant sorption and immobilization due to enhanced surface complexation (**Section 5.2**).

The atomic H:C ratio is often regarded as an indicator for biochar's carbon compound aromaticity, with high ratios associated with low aromaticity [52, 104]. Chemical oxidation and acidification with H_2O_2, HNO_3 and H_2SO_4 can increase aromaticity through dissolution of labile aliphatic carbon, while wet-dry and freeze-thaw cycles usually cause little change to biochar aromaticity (**Figure 3c**). In general, chemical modification with LMWOAs renders the closest H:C ratio changes compared to natural aging, while the use of harsh oxidants such as H_2O_2, NaClO, HNO_3 and H_2SO_4 can lead to severe over-oxidation and inaccurate representation of natural aging (**Figure 3c**).

Cation exchange capacity (CEC) is a measure of biochar's ability to hold positively charged ions, including nutrients or soil contaminants. It also serves as a way to measure biochar oxidation, with greater sensitivity than the O:C ratio [77]. For example, an aging induced change from phenol to ketone groups will not alter the O:C ratio, but will increase the CEC value [77, 105]. In general, aged biochars

usually display higher CEC values than fresh biochars, which can be attributed to surface oxidation [52, 77, 106, 107]. One study reported a CEC decrease after aging (from 19.8 to 1.1 cmol/kg) [108].

The anion exchange capacity (AEC) is also an important measurement. The AEC value relates to the nutrient retention capability of biochar and its capacity for anionic contaminant sorption [109, 110]. Anion exchange sites include oxonium groups (sp^2-O heterocycles), protons electrostatically adsorbed by π-electrons of aromatic rings, and protonated pyridimium groups (N heterocycles) (**Figure S3**) [110]. Decreased AEC values have been observed for biochar after natural aging and after artificial aging with $NaOH/H_2O_2$. A drop in the AEC value may stem from the loss of formal charge on O^+ as a result of oxonium reduction to ether induced by hydroxyl radical [108]. While a decrease in biochar pH would not necessarily affect oxonium groups, it may increase the positive charge density of N heterocycles, and, therefore, release more protons for electrostatic adsorption [108]. An increase in biochar CEC with aging promotes soil fertility in the long run (**Section 5.1**). An elevation in CEC is helpful for the retention of metallic cations (such as copper [111], zinc [112], cadmium [113] and lead [114]), while the decrease in AEC will not be favorable for the immobilization of oxyanions (such as arsenic [115] and chromium [116]).

At the molecular level, biochar can change significantly due to aging processes (**Figure S4**) [52]. For example, aromatic moieties can become disconnected due to the degradation of the labile aliphatic chains that connect them [52]. These aromatic rings will be oxidized, and O-containing functional groups (e.g., hydroxyl, carboxyl, carbonyl) will form on the biochar surface (resulting in increased O/C ratio). With progressive aging, aromatic moieties can fragment into smaller compounds with benzene polycarboxylic acids (BPCAs) eventually forming [117-119]. The full transformation of large aromatic moieties into small BPCAs may take hundreds to thousands of years. In Amazonian Terra Preta soils, biochar produced ~800 years ago has been discovered to now be mainly composed of ~6

fused benzene rings substituted by carboxyl groups with negative charges (COO^-) [52, 120]. In extreme cases, molecular benzene ring with six carboxyl groups will form (B6CA), which will take a very long time (i.e., > 1000 years) [52, 120]. For more information regarding the carbon chemistry of aged biochars, we refer readers to Mia et al. [52].

It is noteworthy that the biomass feedstock, pyrolysis conditions and field characteristics will affect the aging process. A detailed discussion on how these factors influence biochar aging and environmental applications is provided in **Text S1** and **Table S1**.

4 ASSESSMENT

Several *in situ* monitoring studies can provide good evidence regarding biochar's temporal evolution within the soil environment. However, because of time constraints, researchers have more commonly attempted artificial aging methods as a proxy for natural aging, thus cutting the study duration (**Table S4**). Natural and artificial aging methods are discussed in the sub-sections below.

412 ### 4.1 Natural aging methods

413 Long-term *in situ* field aging is the most direct way to observe biochar aging. Recovering biochar
414 particles from the field, by hand-picking or the use of physical separation methods, allows the aged
415 biochar properties to be assessed. Among the literature reviewed, the longest field trial duration was
416 9.5 years (**Table S4**). Such field trials, however, are few and far between due to impracticalities of
417 such studies. Researchers often prefer to incubate biochar-soil mixtures in pot-based studies with
418 constant moisture and humidity. However, pot studies cannot accurately simulate outdoor factors such
419 as rainfall, temperature variance, sunlight. An alternative approach for studying long-term aging
420 effects is to collect biochar that was produced by known historic natural events such as wildfires [121]
421 or at former kiln sites [122].

422 ### 4.2 Artificial aging methods

423 Considering the fact that natural aging is a slow process, artificial aging methods, such as physical
424 aging (e.g., freeze-thaw, wetting-drying), chemical aging (e.g., chemical oxidation, organic acid
425 modification) and biological aging (e.g., co-composting) have emerged as alternatives to natural
426 biochar aging (**Table S4**). These methods help shorten the aging duration from years to months or
427 days.

428 #### 4.2.1 Physical aging

429 Temperature and moisture are important factors in physical aging [51, 123, 124]. For example, in middle-
430 to-high latitude regions, freeze-thaw cycles can leads to the disintegration of biochar-soil aggregates
431 and the release of dissolved organic matter (DOM), thus affecting soil metal leaching and nutrient

transformation [25, 123]. Two common physical aging methods that are used to simulate the aging effects of temperature and humidity are freeze-thaw cycling and wet-dry cycling.

In freeze-thaw cycling studies, selected freezing temperatures range from -70 °C to -15 °C (**Table S4**). While the use of extremely low temperatures may accelerate the aging process, higher freezing temperatures are usually adopted in order to better represent the natural environment. Wet-dry cycles are known to cause cracking on biochar surfaces, thus leading to changed pore structure [124, 125]. This cracking, however, may be an artifact of oven-drying at high temperature (i.e., up to 60 °C). Moreover, freeze-thaw and wet-dry aging methods may not be as representative as chemical and biological aging at mimicking natural aging processes [126].

4.2.2 Chemical aging

Three common approaches that are used to accelerate chemical aging are chemical oxidation, organic acid-induced aging, and photocatalytic oxidation. These methods simulate the effects of inorganic ions, root exudates, and sunlight irradiation on biochar, respectively. One study has also put forward a mineral aging method to assess the effects of clay minerals on biochar physicochemical properties [42].

Peroxide (H_2O_2) is a widely used oxidant for simulating natural oxidation processes in biochar aging studies [126]. The use of nitric acid (HNO_3) or sulfuric acid (H_2SO_4) should generally be avoided to prevent exogenous elements being introduced (e.g., N from HNO_3, S from H_2SO_4) [126]. However, these substances can be used to simulate acid rain, since the major anions in acid rain are NO_3^- and SO_4^{2-} [74]. $NaOH/H_2O_2$ can be used to simulate oxidation reactions in saline-alkali soils [127]. Organic acids, such as citric acid, malic acid and ethanoic acid, can be used to simulate the role of plant root exudates in biochar aging [28]. Carboxylic groups and the ionizing protons of low molecular weight

organic acids (LMWOAs) can dissolve minerals in the rhizosphere [35, 128]. This deashing process may improve the pore structure of biochar by clearing pores that are blocked with Ca-, Al-, or Fe- minerals [28, 129].

On the basis of organic acid-induced aging, a novel photocatalytic aging method was recently proposed. Under UV irradiation, hydroxyl radicals (·OH) with the presence of LMWOAs (e.g., citric acid, H_3Cit) act as the dominant mechanism for biochar degradation and subsequent dissolved organic matter (DOM) release (Eq. 3-6) [27]:

$$H_3Cit + O_2 + h\nu \rightarrow H_3Cit \cdot^+ + O_2 \cdot^- \quad (3)$$

$$H^+ + O_2 \cdot^- \rightleftharpoons HO_2 \cdot \quad (4)$$

$$2HO_2 \cdot \rightarrow H_2O_2 + O_2 \quad (5)$$

$$H_2O_2 + h\nu \rightarrow 2 \cdot OH \quad (\lambda < 300\ nm) \quad (6)$$

Considering that Fe is the fourth most abundant element in soil, ferric iron and α-Fe_2O_3 may also be added to the citric acid solution with biochar, which accelerates the generation of ·OH through a Fenton reaction.

4.2.3 Biological aging

Microorganisms and plants play important roles for biochar aging. Co-composting and anaerobic fermentation are relatively quick methods (e.g., several weeks) to observe microbial degradation effects [29, 86]. However, the microbial communities in these systems are quite different from those found in natural soil environments. Another feasible biological aging method is to culture and enumerate soil microorganisms and apply them directly to biochar surfaces. In one study, for example,

biochar was exposed to a microbial inoculum that had been extracted from soil after a period of incubation [77].

Although mixing biochar with organic acids can mimic the effect of plant exudates on biochar properties, this chemical aging method overlooks the more complex role of rhizobacteria in biochar aging. Growing plants in biochar amended soils may be a better aging approach in this sense, but it can take months or years to accomplish the aging process [130, 131].

5 IMPLICATIONS

5.1 Soil Fertility

Long-term aging of biochar improves soil fertility from physical, chemical, and biological aspects. Firstly, an increase in surface hydrophilicity as a result of oxidation leads to enhanced water retention for aged biochars [132, 133]. For instance, six months of field aging promoted the water retention of rice husk biochar amended soils, as confirmed by the increase of plant available water content by 20% during the second growing season of wheat compared with the soils in the first growing season [134]. Aggregate stability is the key factor in terms of soil physical fertility. High stability of soil aggregates indicates the preservation of soil physical structure for gas exchange, microbial colonization, germination and rooting of cultivated plants [135-137]. Long-term soil aggregate stability improvement has also been observed after biochar field application. For instance, 3-year application of straw biochar to a Planosol increased the proportion of stable aggregates by 92% compared with the unamended soil [138]. It has been acknowledged that the initial biochar application would elevate soil EC via a considerable input of soluble salts [139, 140], thus favoring the aggregation of soil colloids through double layer suppression [141, 142]. In the long run, however, other aggregation mechanisms,

495 such as excretion of mucilage and the attachment of hyphae by colonized bacteria and fungi, would
496 sustain the soil aggregate sustainability despite the leaching of soluble salts [138, 143, 144].

497 The gradual increase in CEC during aging (**Section 3.2**) promotes soil fertility chemically. An
498 increased retention of cationic nutrients, such as Mg^{2+}, K^{+}, and Ca^{2+}, has been observed in many
499 biochar amended soils that have undergone aging over time [52, 145, 146]. The extremely high fertility for
500 anthropogenic charcoal-rich soils are mainly explained by the increase of CEC during natural aging
501 [52, 117, 147]. For instance, the CEC value of the anthropogenic soils collected from an archaeological site
502 in Brazil was nearly 4 times that of the adjacent soils (i.e., 222 cmol/kg vs 59 cmol/kg) [147]. Mild
503 oxidation results in an increase of oxygen-containing functional groups, thus increasing the surface
504 charge density of aged biochars. The adsorption of dissolved organic carbon also contributes to CEC
505 elevation [52, 147]. Furthermore, the dissolution of biochar minerals can be a source of plant nutrients
506 and increase soil fertility directly (**Section 2.1**) [148].

507 Current studies suggest that long-term biochar application could also improve soil health via
508 increasing the diversity of soil microorganisms, which is possibly due to the aforementioned
509 improvement in soil physical and chemical conditions. The alpha diversity (i.e., the Chao 1 index) of
510 wheat straw biochar amended soils increased by 27% compared with the unamended soils after 6
511 years of long-term aging. This is because the formation of stable macroaggregates created an ideal
512 habitat for microbial colonization [149]. A recent meta-analysis also suggest that the microbial diversity
513 tend to increase with biochar aging [150]. One study even observed the colonization of plant-growth
514 promoting bacteria (PGPBs) strains (formation of biofilms) after 3-year field aging of poplar biochars.
515 High levels of indole-3-acetic acid (IAA), a typical phytohormone, can be produced (up to 94 mg/L),
516 suggesting a strong plant growth promoting effect [44].

5.2 Soil remediation

Aging may either increase or decrease biochar's capacity to sorb heavy metals and organic contaminants (**Table S5**). Generally, chemically or biologically oxidized biochars tend to adsorb greater amounts of heavy metals due to enhanced surface complexation between metals and O-containing functional groups [27, 29, 93, 151]. Naturally aged biochars tend to have improved metal adsorption capacity because mild oxidation retains the biochar ash content, thus facilitating contaminant co-precipitation (**Figure 3b**). In comparison, physically aged biochars tend to display decreased adsorption capacity, primarily because they possess low amount of O-containing functional groups and inorganic minerals are washed off during freeze-thaw or wet-dry cycles, thus leading to diminished co-precipitation capability [38, 93, 152]. The adsorption capacity of chemically aged biochars is highly dependent on the biochar carbon chemistry. For example, if the proportion of recalcitrant C is high, the enhanced surface complexation adsorption due to the addition of O-containing functional groups may be counteracted by decreased contaminant co-precipitation due the removal of minerals. Biologically aged biochars may display increased adsorption capacity due to mild oxidation, but this can be counteracted by microbial layers on the biochar surface that block available adsorption sites.

Biochar aging in the field may have diverse influences on metal immobilization performance. Several studies have reported concerns that biochar did not stabilize heavy metals in the long-term. For instance, artificial wet-dry aging showed biochar failed to immobilize soil Cu and Pb for 14 aging cycles ($p > 0.05$) [153]. However, other studies have suggested that aged biochar may favor long-term metal stabilization due to the increased number of O-containing functional groups leading to greater surface complexation (Eq. 7-8) [154, 155]

$$\equiv \mathrm{XOH}^{0} + \mathrm{M}^{2+} = \equiv \mathrm{XOM}^{+} + \mathrm{H}^{+} \quad (7)$$

$$\equiv XOH^0 + M^{2+} = \equiv XOHM^{2+} \quad (8)$$

where $\equiv XOH^0$ represents the surface O-containing functional groups, M^{2+} represents the divalent metal cations.

Contradicting findings in different studies may owe to the counter effects of O-containing functional group-assisted immobilization and dissolved organic matter (DOM)-induced mobilization [131, 156]. In a 3-year field study, for example, Cd and Cu contaminated soils were stabilized in the long-term by corn straw-derived biochar, while the performance of hardwood-derived biochar reduced after the second year [157]. This finding was attributed to the fact that hardwood biochar contains more recalcitrant C which resists oxidation aging. The addition of O-containing functional groups on the hardwood biochar was discovered to be minimal compared to the corn straw biochars.

The addition of O-containing functional groups during biochar aging may affect organic contaminant adsorption in various ways. Firstly, these functional groups increase the hydrophilicity of the biochar surface, forming water clusters through hydrogen bonding. These clusters may prevent hydrophobic contaminants (e.g., naphthalene, paraquat, phthalates) from approaching the biochar surface [70, 158]. Secondly, O-containing functional groups may promote π-π EDA interactions because of increased π-polarity in biochar aromatic rings [158, 159]. Any shift in organic contaminant adsorption capacity with biochar aging is the combined effect of these two mechanisms.

Ghaffar et al. [158] has found that the π-π EDA interactions overcompensated the inhibiting effects of water clusters, resulting in higher adsorption capacity towards diethyl phthalate (68.2 mg/g vs 36.3 mg/g) and dibutyl phthalate (216.1 mg/g vs 136.0 mg/g) for chemically oxidized low temperature biochar (pyrolysis temperature 300 °C). Similarly, Shi et al. [70] noticed that naturally aging resulted in a substantial increase in herbicide paraquat adsorption capacity (from 1.7 μmol/g to 5.3 μmol/g) for

561 biochar pyrolyzed at a low temperature (i.e., 300 °C). However, the adsorption capacity decreased
562 (from 84.1 μmol/g to 72.0 μmol/g) for biochars produced at a much higher temperature (i.e., 600 °C).
563 This effect may be explained by the different carbon chemistry of biochars produced at different
564 temperature. Low-temperature biochars possess more labile C, while higher-temperature chars have
565 more graphite-sheet structures with high π-electron density (**Text S1**, **Table S1**) [9, 160]. Therefore,
566 oxygenation of high-temperature biochar may not cause a significant drop in π-electron density to
567 support the presence of π-π EDA interactions [159].

568 Current findings suggest that biochar aging may not favor the immobilization of organic
569 contaminants. Decreased physical adsorption due to blockage of pore, inhibited hydrophobic
570 interactions and the mobilizing effect of soil organic matter (SOM) may account for the diminished
571 stabilization [161, 162]. In one study, the phenranthelene adsorption capacity of a soil amended with pig
572 manure-derived biochar increased after aging [163]. This finding was probably because manure-derived
573 biochar possessed more inorganic minerals (i.e., high ash content) compared with other biochar types
574 [9]. The hydrophilic groups of dissolved organic carbon (DOC) may bind with inorganic minerals (to
575 form cation bridges), while the hydrophobic groups of DOC will be exposed on the outer surface of
576 biochar, thus favoring the hydrophobic interactions. Therefore, aged biochars could adsorb organic
577 contaminants in an indirect way (i.e., contaminant-DOC-cation-biochar) [163].

578 It is also noteworthy that biochar aging may favor the microbial degradation of organic
579 contaminants. After microbial colonization on the external and internal surfaces as a result of
580 biological aging (**Section 2.4**), biochar may act as an electron shuttle between these colonized
581 microorganisms and the organic contaminants. Electrons can be transferred from one microbial cell
582 to the functional groups with an electron-accepting capacity (e.g., quinone). After that, the sp^2-
583 hybridized graphite-like structure of biochar could transport the electron to an electron-donating

584 functional groups (e.g., phenolic hydroxyl), which will be accepted by the target contaminant [164-166].
585 With progressive aging, the presence of more oxygen-containing functional groups (**Section 3.2**) of
586 biochars may promote this "electron shuttle" effect. Future studies are needed to verify how biochar
587 would contribute to the adsorption/degradation of organic contaminants in the long run.

588 **5.3 Climate change mitigation**

589 Controversy exists whether biochar field aging can suppress soil greenhouse gas (GHG) emissions
590 (**Figure S6**). [167]. Evidence from long-term field applications (i.e., >1 year) suggest that biochar can
591 slightly suppress soil CO_2 emissions (reduce CO_2 emissons by 2% on average, compared with the
592 unamended soil) (**Figure S6**, **Table S6**). Biochar was the most effective for CO_2 emission mitigation
593 in coarse-textured soils, with significant differences (p<0.05) between soil CO_2 emission reduction
594 rates for sandy loam and clay loam (**Figure S6**, **Table S6**). This is probably because biochar are more
595 likely to form water-stable aggregates in coarse soils [138, 168], which will protect soil organic matter
596 (SOM) from mineralization [169, 170].

597 A long-term field trial (9.5 years) revealed a negative priming effect within the rhizosphere in soils
598 amended with biochar, which was related to the sorption of root exudates by the biochar, hence
599 minimizing C mineralization through inhibiting the dissolution of SOM. Biochar addition may also
600 enhance organo-mineral interactions which result in C stabilization and, therefore, lower CO_2
601 emissions (**Figure 4**). In comparison, a positive priming effect in unamended soil stems from
602 chemically reduced C (i.e., root exudates) stimulating the degradation of SOM and C derived from
603 plant roots, thus leading to C mineralization and CO_2 emissions. In addition, acidic root exudates also
604 lead to the dissolution of mineral-bound organic C, thus increasing the bioavailability of SOM
605 (**Figure 4**). However, some studies have observed a reverse trend, that long-term biochar application

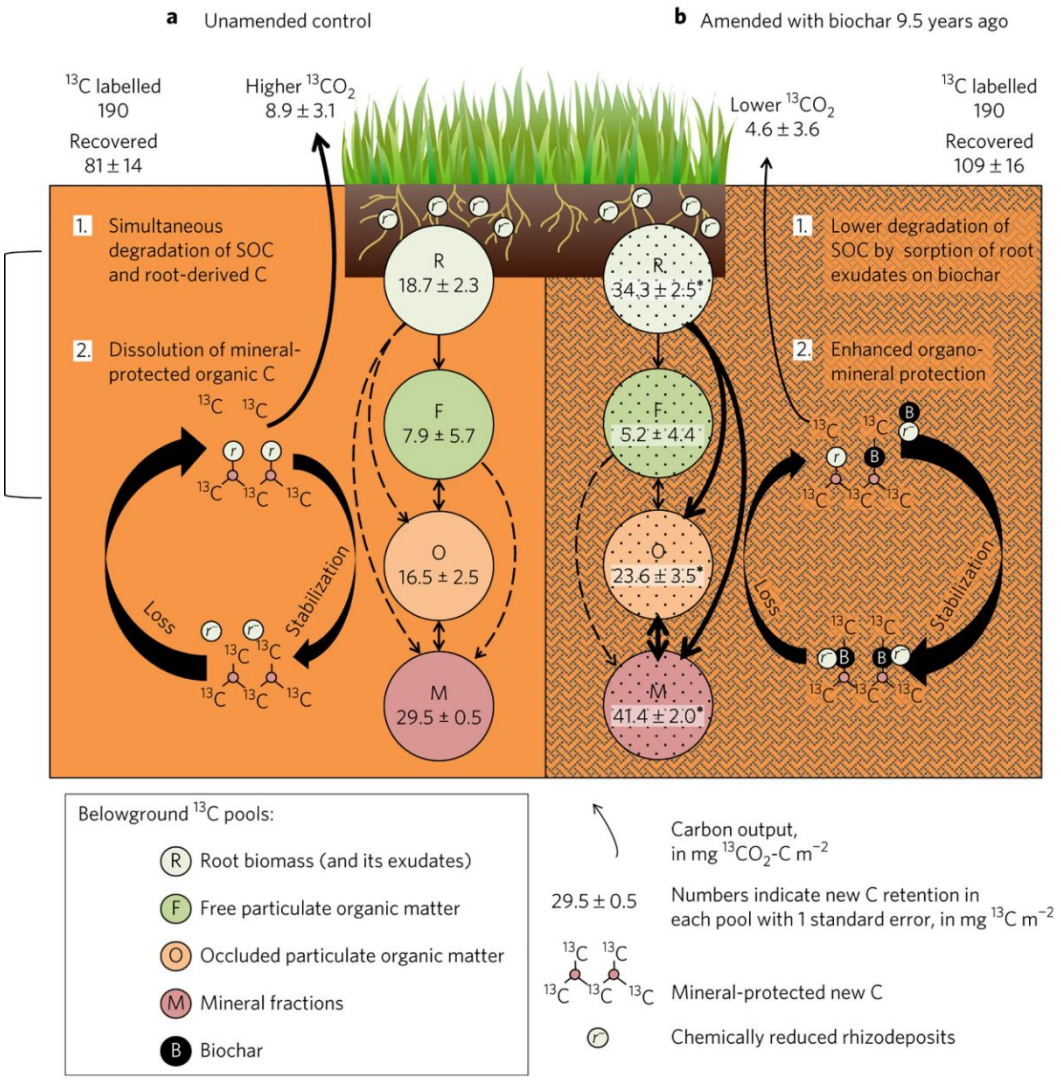
606 led to more CO_2 emissions from soil (**Table S6**). This may stem from the rapid colonization of soil
607 microorganisms and biological degradation increased the soil labile organic C pools [171] and
608 accelerated SOC mineralization [172].

609 Long-term aging can also reduce CH_4 emissions from soils amended with biochar (**Table S6**).
610 Biochar applied to a paddy field could still reduce CH_4 emissions by 33% even after 4 years of natural
611 aging. Interestingly, a higher application rate (i.e., 20 t/ha vs 5 t/ha) will not be equal to higher CH_4
612 emission reduction at the initial stage until the second year. With progressive aging, the positive
613 effects of biochar application on soil health, such as the enhanced aeration and colonization of
614 methanotrophs, will be revealed. Another 4-year field study showed that after biochar application, the
615 ratio of methanogens to methanotrophs increased to a peak in the 3rd year from 4.4 to 9.4 (calculated
616 by the copy number ratios of *mcrA* to *pmoA*) and then subsequently decreased to 4.6 in the last year
617 [173]. This temporal pattern was likely associated with biochar aging leading to increased soil porosity
618 and air introduction, which increased the oxidation-reduction potential (Eh) and, thus, reduced the
619 abundance of methanogens.

620 Biochar aging also affects soil N_2O emissions by influencing microorganism activity associated
621 with nitrification and denitrification. A long-term study of the effects of biochar aging (6 years) on
622 nitrification-denitrification in paddy soil and associated N_2/N_2O emissions revealed decreased C and
623 N bioavailability, with decreasing amounts of NO_3^- reduction and total N emissions recorded. After
624 aging for 6 years, the labile C forms in the biochar decreased substantially, while the remaining
625 recalcitrant C forms could not be utilized by most denitrifying microbes [174]. Another study reported
626 the reverse trend, revealing that biochar aging stimulated N_2O emission by 43% in alkaline soils and
627 by 78% in acid soil [175]. The enhanced nitrification and denitrification were the main reason for this
628 stimulation.

629 The underlying mechanisms involved in suppression or stimulation of GHG emission with biochar
630 aging have not yet been fully addressed. The linkages between biochar characteristics, soil properties,
631 and microbial communities on C and N transformation rates should be further explored. In particular,
632 more field studies should be conducted to explore the roles of soil aggregation, microbial colonization,
633 organic acid and mineral adsorption in GHG emission regulation in-depth.

634



635

Figure 4. Proposed mechanisms for positive rhizosphere priming of soil organic carbon (SOC) counteracted by biochar-induced negative priming and stabilization of rhizodeposits in a ferralsol after 9.5 years. Reproduced with permission from Han Weng et al. [167]. Copyright 2017 Springer Nature.

6 FINAL CONSIDERATIONS

6.1 Risks associated with biochar aging

Biochar aging can lead to an acidification effect, which may mobilize soil metals and increase their bioavailability to soil organisms and plants (**Figure 3b**). For instance, although fresh biochar application can reduce Al^{3+} uptake to plant tissues in acidic soils through a "liming" effect, biochar acidification due to long-term field aging could increase the exchangeable aluminum fraction [176]. Root exudates (consisting of LMWOAs) which facilitate the dissolution of biochar nutrients (e.g., $K_2Ca(SO_4)_2$, $K_2Mg(PO_3)_4$, $CaCO_3$), may also facilitate the mobilization of potentially toxic elements, due to the dissolution of Al- and Pb-containing minerals (e.g., $Al(H_2PO_4)_3$, $AlPO_4$, $Pb_2(SO_4)O$, $Pb_2P_2O_7$) [28]. Biochar aging may also increase the release of DOC leading to nutrient loss and metal mobilization.

Recent studies have shown that aging could increase the mobility of small (colloidal) biochar particles in the subsurface, leading to nutrient loss and contaminant migration in biochar amended soils. It has been suggested that biochar aging can decrease biochar hydrophobicity and shift the Gibbs free energy from negative to positive [94]. This indicates that Lewis acid-base interactions between biochar colloids and soil would shift from attractive to repulsive (i.e., hydration force) thus enhancing biochar particle migration. Therefore, aged biochar may pose a risk to groundwater, since heavy

metals, herbicides, microplastics and even pathogens (e.g., bacteria and viruses) may transport with biochar colloids [177, 178].

6.2 A framework for long-term field applications

To better comprehend the role of long-term biochar field application in sustainable agriculture, a DPSIR (driving forces – pressures – status – impacts – responses) framework is proposed (**Figure 5**). Although DPSIR has been commonly used to describe the interactions between society and the environment, extrapolating this framework to biochar field application can help better understand the interrelationships between aging-induced changes and soil fertility, remediation, and climate change mitigation. Firstly, the demand on producing more crops and remediating contaminated soils are the drivers for biochar application in the field (drivers). After biochar addition, various natural forces, such as natural oxidation, microbial metabolism, and rainfall events lead to changes in biochar physicochemical properties (pressures). Consequently, biochar will be oxidized and acidified, and more O-containing functional groups will be introduced onto its surface. Furthermore, biological aging of biochar may form a microbial layer, blocking the pores structure (status).

Biochar aging can either positively or negatively affect sustainable agriculture. On the one hand, biochar aging delivers sustained slow release of nutrients that promote soil fertility in the long run. Enhanced surface complexation also favors the long-term immobilization of potentially toxic soil metals. Importantly, biochar aging can decrease GHG emissions due to a negative priming effect and changed abundance of methanogens and methanotrophs. On the other hand, long-term biochar aging may cause acidification which increases the mobility of potentially toxic soil metals. It has also been suggested that biochar aging can enhance biochar particle migration and facilitate the transport of herbicides and other potentially harmful substances (impacts).

To meet the growing demand for increased crop production, soil remediation and climate change mitigation, chemical pre-application aging treatment may offer a feasible approach to improved performance (response 1). To better understand the mechanisms associated with long-term aging of biochar, monitoring of biochar amended soils is necessary (response 2). To predict aging-induced changes in biochar properties, developing quantitative accelerated aging tests is needed (response 3).

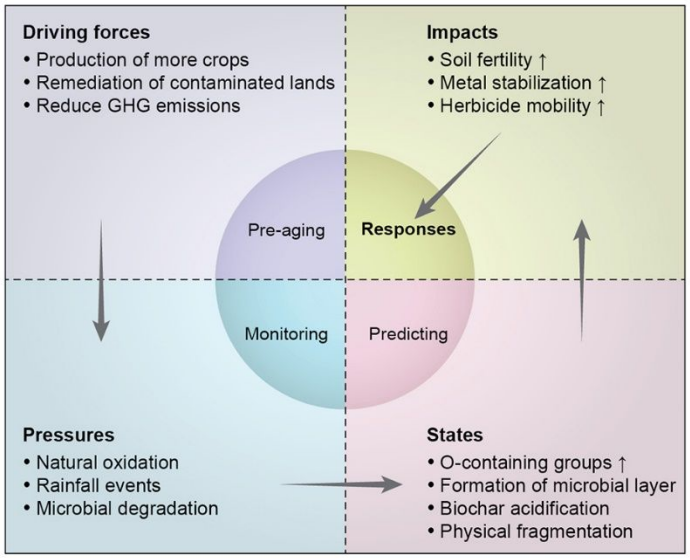


Figure 5. A DPSIR framework for long-term biochar applications. Chemical pre-application aging treatment (pre-aging), long-term monitoring and prediction using quantitative artificial aging approaches can be regarded as responses to the driving forces, pressures and the states, respectively. To meet the demand on crop production, soil remediation and climate change mitigation, chemical pre-application aging treatment can act as an effective tool to produce engineered biochars with excellent performances (i.e., contaminant immobilization, fertility improvement and GHG mitigation). To better understand the mechanisms associated with long-term aging of biochar, monitoring of biochar amended soils is necessary. To predict aging-induced changes in biochar properties, developing quantitative accelerated aging tests in the laboratory is a feasible way.

6.3 Current challenges and future perspective

Long-term monitoring of biochar-amended soils provides direct evidence on how this soil amendment changes with time. However, due to the time constraints, more studies have developed artificial aging methods as proxies. Existing methods have mainly focused on single aging mechanisms, meaning that they do not represent the complex natural conditions of the real world. Moreover, chemical aging with oxidants tends to cause over-oxidation compared to natural aging, especially when strong oxidants are used. Furthermore, exogenous elements may be introduced to the biochar from certain chemicals (e.g., N from HNO_3, S from H_2SO_4) [126].

The effects of artificial physical aging are limited to only the biochar porous structure with no significant changes to the ultimate properties. The freezing temperature selected for freeze-thaw cycling can be unrealistic low (e.g., below -20 °C). In addition, the drying part of wet-dry cycles usually involves higher temperatures (e.g., 60 °C) than that typically occur in nature, leading to biochar cracking. While biological aging may be much milder than chemical oxidation, the microorganisms used may follow different metabolism pathways (e.g., co-composting) than a soil microbiome.

Since natural aging is a complex process that involves simultaneous physical, chemical and biological aging mechanisms, future studies ought to develop multifaceted advanced aging methods that combine different mechanisms. New methods could be programed to have variable aging stresses with time. For example, wet–dry and freeze–thaw cycling could be conducted with variable temperatures, frequencies, precipitation levels, and freeze periods. Climate change predictions could be applied to aging methods in order to determine biochar's resilience [179]. When it comes to the

715 selection of chemical oxidation agents, we recommend that mild natural oxidants are used (e.g., citric
716 acid, malic acid as root exudates).

717 Field monitoring is very important to timely assess the function of biochar. It is suggested to carry
718 out periodically sampling and analysis to verify the performance of biochar in fertility improvement,
719 contaminant remediation and GHG emissions mitigation. In-situ wireless sensors detecting the
720 moisture content, pH, Eh, and conductivity of biochar-amended soils can be used to provide real-time
721 monitoring and help assess the potential environmental impacts on biochar. In addition, advanced
722 characterization technologies could be coupled with long-term monitoring to provide a timely "health
723 assessment" of biochar and the amended soil. For example, stable isotope analysis can reveal the
724 nutrient cycling and GHG mitigation mechanisms of the biochar-amended soils. X-ray absorption
725 fine spectra can reveal the speciation of elements, including biochar carbon chemistry and the
726 chemical composition of the adsorbed contaminants, therefore suggesting the effectiveness of
727 environmental remediation in the long-run.

728 Since biochar can remain stable for hundreds to thousands of years, it is not possible to conduct
729 field trials that cover the whole natural aging process. Sometimes applying fresh biochar to a certain
730 field and monitor for dozens of years may also be difficult due to various reasons including the cost,
731 land-use regulations, natural disasters, etc. Yet it is possible to monitor the aging process using
732 chrono-sequence approaches, that is, to collect data from different biochar-amended sites with
733 different ages and analyze their aging characteristics using statistical approaches.

734 Quantitative artificial aging methods in the lab should be applied to make predictions of biochar's
735 long-term performance. However, only limited attempts have been made at providing quantitative
736 information from accelerated biochar aging. In some studies, biochar aging caused by natural rainfall

has been quantified through adding calculated amounts of CO_2-saturated water to biochar amended soils [180, 181]. For example, assuming the annual precipitation is 2 m, each 1 g of dry soil (density = 1.3 g/cm^3) would receive 1.538 mL of pH 5.6 rainwater per year. Therefore, it is reasoned that each cycle involving a 1:10 mixture (g/mL) of soil and rainwater simulates 6.5 years of H^+ addition. Another suggested quantitative approach combined wet-dry cycles with freeze-thaw cycles to simulate the different mechanisms of aging [26]. Based on historical precipitation and air temperature data, it was proposed that each complete cycle simulates four months of natural aging. It is evident that such partially quantitative methods may not provide accurate predictions, since many other factors, such as sunlight irradiation, chemical oxidation and microbial metabolism are overlooked. Moreover, verification of laboratory aging studies with representative field data obtained from the long-term monitoring or chrono-sequence analysis is urgently required.

It is also noteworthy that current studies mainly focus on the aging process in terrestrial ecosystems. However, many successful attempts have shown that biochar can also be applied in aquatic ecosystems as an amendment for *in situ* sediment remediation [182-185]. Little research, however, has investigated the long-term aging effect in these systems [186, 187]. Future studies are desperately needed to explore the aging mechanisms in these aquatic settings.

Artificially pre-aged biochars promise to be more effective for field applications than fresh biochar. In this context, artificial aging acts as a tool to synthesize an engineered biochar product (**Figure S5**). For enhanced contaminant immobilization, harsh oxidants, such as H_2O_2, H_2SO_4 and HNO_3 may be an effective aging approach (**Figure 3d**). For soil fertility improvement, modifying biochar with LMWOAs may be more effective. It is suggested that future studies should explore the applicability of pre-aged biochars in field trials.

759

760 **ASSOCIATED CONTENT**

761 **Supporting Information:**

762 Text S1. Effects of biomass feedstock, pyrolysis conditions and field characteristics on biochar
763 aging. Table S1. Influencing factors affecting the aging process and environmental implications.
764 Table S2. Aging-induced changes in biochar morphology and associated physico-chemical changes.
765 Table S3. Aging induced changes in biochar properties. Table S4. Natural and artificial approaches
766 to biochar aging. Table S5. Contaminant adsorption performances of aged biochars. Table S6. Field
767 evidence for biochar's ability to mitigate GHG emissions in the long run. Figure S1. Evidence of
768 physical fragmentation as an aging mechanism. Figure S2. N_2 adsorption-desorption isotherms of
769 fresh and aged biochars revealing the changes in pore structure. Figure S3, Anion exchange
770 mechanisms for biochars. Figure S4. A molecular understanding of changes in biochar chemical
771 compositions upon aging. Figure S5. Effects of biochar aging on contaminant retention, soil fertility
772 and climate change. Figure S6. Box plots revealing the effects of long-term biochar application on
773 soil CO2 emissions.

774

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778 Notes

779 The authors declare no competing financial interest.

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