Amendment A to Global Biochar C-Sink Standard 3.2

Version 0.9 (final review pending), valid from 22.12.2025

Persistence evaluation for highly condensed biochar Introduction of the Upper Persistence Class of Biochar

A1.1 Polycondensed aromatic structure of biochar

The principal structure of biochar consists predominantly of aromatic rings composed of six carbon atoms. These rings are fused in clusters of varying size and complexity. The stability of biochar mainly depends on the degree to which aromatic rings are condensed (i.e., fused together) and on the architecture in which these condensed structures are organized. The biological and chemical stability of biochar increases with its degree of aromaticity and the extent of ordered aromatic ring condensation (see A1.5 Glossary for the Amendment below).

While no biochar carbon fraction can be regarded as completely inert, increasing aromatic condensation substantially reduces the probability of biological or chemical degradation (Schmidt et al., 2025). Biochar carbon fractions dominated by highly condensed aromatic structures exhibit a markedly increased likelihood of surviving for more than 1000 years after application to soil, as supported by observations of ancient charcoal and pyrogenic carbon persisting over millennial timescales in soils and sediments (Howell et al., 2022). Persistence beyond this timescale is commonly interpreted as a transition from the fast and intermediate terrestrial carbon cycle into the geological carbon cycle (Schmidt and Noack, 2000). Biochar carbon that reaches millennial persistence can therefore be considered a geological carbon sink, acknowledging that this classification reflects a probabilistic assessment of long-term stability rather than absolute permanence (see Chapter 2.2 of the Global Biochar C-Sink Standard).

A1.2 The probabilistic approach

The Global Biochar C-Sink Standard does not define a discrete physical biochar fraction that is assumed to persist without degradation and thus be inert for more than 1000 years. Instead, it distinguishes between two conceptual carbon pools based on persistence probabilities. The persistent aromatic carbon (PAC) fraction is defined as the portion of biochar carbon that is expected to survive for more than 1000 years after application to soil, whereas the semi-persistent carbon (SPC) fraction comprises the portion of biochar carbon that is expected to degrade within the first 1000 years.

Aging of biochar in soil is not only characterized by slow biological and chemical degradation processes but also by physical and chemical stabilization mechanisms (Lehmann et al., 2024). Biochar longevity is therefore determined not only by its polyaromatic structure but also by environmental factors such as soil mineralogy, biological activity, and climatic conditions. With increasing residence time in soil, the probability that biochar carbon becomes physically and chemically protected increases. Mineral-associated stabilization may allow pyrogenic carbon to be preserved over very long timescales, even when its molecular structure is less aromatic or partly degraded (Schmidt et al., 2025).

Both the PAC and SPC fractions consist of a continuum of aromatic structures with varying degrees of condensation. While any fraction may become physico-chemically protected in soil, the probability that a given aromatic cluster persists for more than 1000 years increases with increasing aromatic condensation and structural ordering. PAC and SPC, therefore, do not represent chemically distinct or sharply separable fractions, but probabilistic pools reflecting different likelihoods of long-term persistence. To estimate the relative size of the PAC and SPC pools for a given biochar based on measurable structural properties, analytical proxies are required.

A1.3 Analytical proxies for biochar persistence

The degree of aromatic condensation represents an average structural property of a biochar sample that integrates a wide range of molecular configurations and condensed aromatic clusters. It cannot be measured directly as a single physical parameter but can be approximated using several analytical proxies that correlate with the extent of aromatic ring condensation.

Historically, the molar hydrogen-to-organic-carbon ratio (H/Corg) has been the most widely used proxy to characterize the degree of aromatic condensation in biochar and to infer its relative persistence. During pyrolysis, hydrogen is preferentially lost as volatile compounds, while carbon increasingly forms aromatic and polycondensed structures. As a result, decreasing H/Corg ratios generally indicate increasing aromaticity (Wiedemeier et al., 2015). This relationship has been demonstrated across a wide range of feedstocks and pyrolysis conditions and has therefore been adopted as a practical, cost-effective proxy for biochar stability (Budai et al., 2016; Woolf et al., 2021).

A key advantage of H/Corg is its empirical linkage to biochar degradation observed in pot and field experiments. Most long-term incubation, pot, and field trials that quantify biochar-derived CO_2 emissions have relied on elemental analysis as part of biochar characterization, making H/Corg the only proxy for which a substantial empirical basis exists across diverse soils, climates, and biochar types. Recent harmonized analyses and re-evaluations of biochar decomposition datasets confirm that H/Corg remains one of the most robust predictors of relative biochar persistence when evaluated against long-term mineralization data (Azzi et al., 2024; Lebrun Thauront et al., 2024).

However, H/Corg represents an average bulk property of a biochar sample and does not resolve the internal heterogeneity of aromatic structures. In particular, it cannot sufficiently account for the influence of mineral ash (Hagemann et al., 2025). High-ash biochars may exhibit elevated H/Corg ratios despite containing highly aromatic and polycondensed carbon structures, due to dilution effects and catalytic interactions during pyrolysis that alter hydrogen retention without proportionally reducing aromatic condensation (Grafmüller et al., 2022). As a consequence, H/Corg may underestimate the persistence potential of ash-rich biochars and does not reliably distinguish between different architectures of condensed aromatic clusters that may differ substantially in long-term stability.

Therefore, while H/Corg provides a conservative and empirically grounded approximation of biochar persistence, its limitations motivate the use of complementary analytical proxies that more directly capture the presence, abundance, and structural organization of highly condensed aromatic carbon fractions.

Hydropyrolysis (HyPy) has been developed as an analytical method to operationally isolate aromatic carbon fractions with a higher degree of ring condensation in biochar by selectively removing labile and less condensed carbon compounds under high-pressure hydrogen at elevated temperatures. The residual carbon fraction obtained by HyPy (BC_{HyPy}) is dominated by aromatic clusters consisting of more than seven condensed rings and is therefore considered a reliable approximation of the more stable biochar carbon pool (Howell et al., 2022). The carbon fraction volatilized under these extremely harsh conditions is operationally defined as the reactive carbon fraction (C_{react}) and is characterized by a substantially lower probability of surviving for more than 1000 years after application to soil.

Solid-state electric conductivity (SEC) has recently been proposed as an additional proxy for aromatic condensation, reflecting the increasing connectivity and delocalization of π-electrons in polycondensed aromatic carbon structures. SEC shows strong correlations with H/Corg and BC_{HyPy} (Hagemann et al., 2025). As SEC is a relatively simple and cost-efficient method that can be measured even at the production site, it has the potential to complement other analytical proxies on a continuous basis (Hagemann et al., 2025).

Random reflectance (Ro) provides a detailed and robust measure of the structural ordering and maturation of aromatic carbon domains at the microscale. The mean Ro value, which is commonly used for persistence-related evaluations, is derived from a large number of individual point measurements across a biochar sample (typically 300–500), thereby capturing its intrinsic heterogeneity. For a single, homogeneous biochar material, the distribution of individual Ro measurements generally follows a Gaussian distribution, with the standard deviation reflecting the internal variability of aromatic condensation. Originally developed in coal petrology, Ro has been adapted for biochar analysis to resolve the spatial variability and degree of aromatic condensation within a single material (Petersen et al., 2023).

At the microscale, higher reflectance values indicate a higher degree of aromatic ordering and polycondensation within a given carbon domain. Ro has been shown to correlate with pyrolysis severity, including temperature, pressure, and residence time, as well as with H/Corg ratios and the relative abundance of more condensed aromatic carbon structures (Sanei et al., 2023, 2025). In addition, emerging datasets indicate strong correlations between Ro, SEC, and the fraction of biochar carbon resistant to hydropyrolysis, further supporting its relevance for persistence assessment.

Unlike bulk elemental proxies, Ro explicitly accounts for the coexistence of differently ordered aromatic domains within a single biochar sample, thereby providing insight into the internal distribution of more- and less-stable carbon structures. Importantly, Ro does not imply chemical inertness or absolute persistence, but serves as a relative indicator of the likelihood that a given fraction of biochar carbon belongs to the more condensed end of the aromatic continuum (Schmidt et al., 2025). In this sense, Ro supports a probabilistic interpretation of PAC and SPC pools and complements both H/Corg and HyPy by resolving structural heterogeneity that bulk and operational proxies cannot capture.

A1.4 The Upper Persistence Class of Biochar

In 2021, the Global Biochar C-Sink Standard introduced two analytical persistence classes based on the molar hydrogen-to-organic-carbon ratio (H/Corg). Biochars with H/Corg < 0.4 are assigned to a persistence class in which 75% of biochar carbon is attributed to PAC and 25% to SPC, while biochars with H/Corg ≥ 0.4 are assigned entirely to the SPC pool. This threshold has been shown to be robust across a wide range of feedstocks and pyrolysis conditions. Within this framework, however, no further differentiation is made among biochars exhibiting very high degrees of aromatic ring condensation, including materials with H/Corg values well below 0.25. As a result, biochars with substantially varying degrees of aromatic condensation and structural ordering are currently grouped within the same persistence class, despite clear evidence of differences in their reactive carbon fractions and long-term stability.

Over the past years, additional analytical methods—most notably random reflectance (Ro) and hydropyrolysis (HyPy)—have generated a substantial and consistent body of data demonstrating higher discriminatory power for identifying biochars with very high degrees of aromatic condensation and structural ordering. These methods enable a more precise identification of biochars in which the reactive carbon fraction is exceptionally low and the probability of millennial-scale persistence is correspondingly high.

Based on this expanded analytical evidence, the present annex introduces a third, preliminary persistence class to capture biochars at the upper end of aromatic condensation and structural ordering. This class resolves differences among highly aromatic materials with molar H/Corg ratios < 0.4 that are not captured by the existing H/Corg-based classification. For the period 2025–2026, certification of the upper persistence class is limited to a maximum of 1,000 tons of biochar that are produced and soil-applied within the "CSI – Inertinite Pilot Project". This quantitative restriction reflects the pilot character of the new class and allows controlled implementation while additional operational and empirical experience is gathered. Following public consultation in the first quarter of 2026, the Global Biochar C-Sink Standard Version 4 is expected to formally integrate the new persistence classification.

Analyses combining Ro, HyPy, and SEC reveal a non-linear transition in biochar structure at high degrees of aromatic ring condensation. In particular, biochars exhibiting a Mean $Ro_{>2\%}$ above approximately 3.8% show a marked and consistent shift across multiple independent indicators. Above this threshold of 3.8%, the fraction of biochar carbon resistant to hydropyrolysis (BC_{HyPy}) consistently exceeds 90%, while the reactive carbon fraction approaches values below 1%. At the same time, SEC increases by more than one order of magnitude, indicating that aromatic cluster connectivity has progressed to a level at which biochar transitions from an electrical insulator to a conductor (publication of SEC data pending). These converging changes indicate that aromatic domains are no longer merely larger, but qualitatively more ordered and interconnected.

The transition observed around a Mean $Ro_{>2\%}$ value of 3.8% reflects a structural inflection point rather than a gradual progression. Beyond this point, further increases in pyrolysis severity lead to only minor changes in reactivity, while ordering and connectivity dominate material behavior. The Mean $Ro_{>2\%}$ threshold of 3.8% represents a conservative, empirically derived boundary at which biochar carbon shifts into a regime characterized by exceptionally low reactivity and a very high probability of millennial-scale persistence. This regime corresponds approximately to molar H/Corg ratios below 0.25, as independently observed in recent datasets (Hagemann et al., 2025; Sanei et al., 2025, 2024).

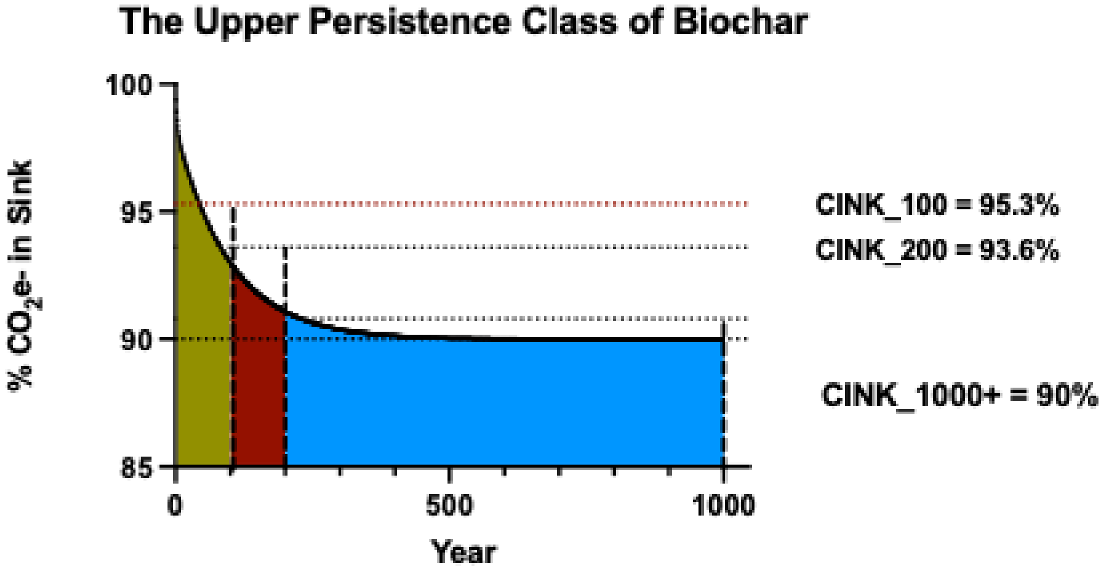

Figure A1. Schematic illustration of the partitioning of biochar carbon into persistent aromatic carbon (PAC) and semi-persistent carbon (SPC) as applied in the Biochar C-Sink Standard. For biochars meeting the new preliminary persistence class (Mean Ro>2% ≥ 3.8% or BC_HyPy > 90%), PAC is conservatively set to 90% of total biochar carbon and treated as a stable fraction persisting beyond 1000 years, *representing transfer into the geological carbon cycle. The remaining 10% is assigned to SPC and follows an exponential degradation function as defined in the Biochar C-Sink Standard. The figure illustrates the persistence allocation and the conservative separation between long-term storage (PAC) and modeled degradation (SPC), rather than spatial or chemical gradients within the biochar material.*

Biochars are assigned to the new upper persistence class if they meet at least one of the following criteria:

(i) a mean random reflectance (of all reflections measurments above 2.0%) ≥ 3.8%,
(ii) a fraction of biochar carbon resistant to hydropyrolysis exceeding 90%.

For Ro-based classification, the following conditions must additionally be fulfilled to ensure that the reflectance data represent a single, homogeneous biochar material. The distribution of random reflectance values shall not display bimodality, as bimodal distributions indicate mixing or heterogeneous production conditions (Figure 2). The fraction of biochar carbon exhibiting random reflectance values below 2.0% shall not exceed 3.0 % of total biochar carbon. The Mean $\mathrm{Ro}_{>2\%}$ value shall be calculated exclusively from individual reflectance measurements equal or exceeding a random reflectance of 2.0%.

Biochars assigned to this upper persistence class are attributed a persistent aromatic carbon fraction (PAC) of 90% and a semi-persistent carbon fraction (SPC) of 10%. This allocation includes a substantial margin of safety, as such biochars typically exhibit reactive carbon fractions well below 10%. Accordingly, the probability that biochar carbon within this class persists for more than 1000 years after application to soil can be conservatively considered to be at least 90%.

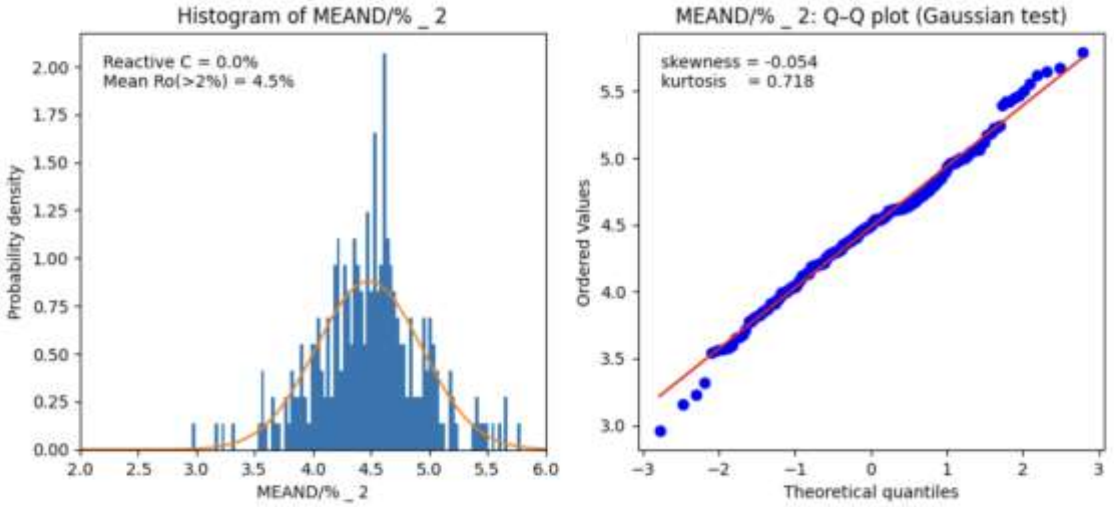

Figure A2. Example of a random reflectance (Ro) histogram showing individual point measurements with Ro ≥ 2% used for the calculation of Mean Ro>2%. The accompanying Q–Q plot compares the empirical distribution of Ro values against a theoretical Gaussian distribution and is used to assess whether the reflectance data are consistent with a unimodal distribution. The absence of bimodality supports the interpretation that the sample represents a single, homogeneous biochar material and does not indicate mixing of biochars produced under differing conditions.

Ro and HyPy are strongly related to aromatic condensation, but differ in analytical nature, availability, and operational constraints. Random reflectance resolves microscale heterogeneity and is particularly effective at detecting mixed production conditions, whereas hydropyrolysis isolates a chemically defined residual carbon fraction associated with higher ring condensation. Both methods independently indicate the same structural transition and show consistent agreement with other persistence-relevant indicators such as H/Corg and SEC. Accepting either criterion, therefore, preserves scientific robustness while enabling practical implementation across different production and laboratory settings. The conservative PAC allocation of 90% ensures a margin of safety regardless of whether classification is based on Ro or HyPy.

Biochars with a mean random reflectance below 3.8% remain eligible for registration under the existing H/Corg-based persistence classification, representing a PAC fraction of 75% for H/Corg < 0.4. The method will be further refined in the next standard update (i.e., 3.2 to 4.0).

A1.5 Glossary for the Amendment

Aromatization, **aromatic ring condensation**, and **structural ordering of aromatic domains** describe complementary aspects of biochar carbon transformation that emerge concurrently with increasing **pyrolysis severity**, while differing in their sensitivity to specific process parameters and analytical proxies. The definitions of the four principal terms are outlined below.

Pyrolysis severity

The combined thermal and chemical forcing of biomass during the pyrolysis process, determined by process parameters such as temperature, heating rate, residence time, and gas pressure or atmosphere in the reactor, as well as catalytic effects of inorganic constituents (e.g., ash and minerals). Pyrolysis severity governs the extent to which biochar carbon undergoes the following chemical and structural transformation.

Aromatization (aromaticity increase)

The conversion of non-aromatic carbon structures (aliphatic and oxygenated compounds) in biomass into aromatic carbon domains during pyrolysis. Increasing aromatization is typically reflected by decreasing molar H/Corg (and typically O/Corg) ratios and a reduction in heteroatom-containing functional groups at aromatic ring edges. More aromatization results in purer aromatic carbon rings with fewer hydrogen, oxygen, and other heteroatom-containing functional groups at the edges of the aromatic structures.

Aromatic ring condensation (extend of ring fusion)

The progressive fusion of aromatic rings into larger clusters (polycondensation) and the shift toward larger polycyclic aromatic structures composed of an increasing number of fused rings. Higher aromatic ring condensation corresponds to larger polycyclic aromatic domains and is associated with reduced chemical and biological reactivity. Hydropyrolysis (HyPy) operationally isolates the carbon fraction of more than seven condensed aromatic rings from less condensed ring structures. Random reflectance (Ro) increases with increasing aromatic ring condensation and reflects the growth and maturation of fused aromatic domains.

Structural ordering of aromatic domains
The increased ordering and maturation of aromatic carbon domains (fused aromatic clusters) with rising pyrolysis severity. Structural ordering includes greater alignment, stacking, and connectivity of polycondensed aromatic structures and enhanced π-electron delocalization. It reflects a transition from disordered aromatic clusters toward more ordered, graphitic-like arrangements and is captured by proxies such as random reflectance and solid-state electrical conductivity.

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