Negligible Quantities of Particulate Low-Temperature Pyrogenic Carbon Reach the Atlantic Ocean via the Amazon River

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Abstract Particulate pyrogenic carbon (PyC) transported by rivers and aerosols, and deposited in marine sediments, is an important part of the carbon cycle. The chemical composition of PyC is temperature dependent and levoglucosan is a source-specific burning marker used to trace low-temperature PyC. Levoglucosan associated to particulate material has been shown to be preserved during riverine transport and marine deposition in high- and mid-latitudes, but it is yet unknown if this is also the case for (sub)tropical areas, where 90% of global PyC is produced. Here, we investigate transport and deposition of levoglucosan in suspended and riverbed sediments from the Amazon River system and adjacent marine deposition areas. We show that the Amazon River exports negligible amounts of levoglucosan and that concentrations in sediments from the main Amazon tributaries are not related to long-term mean catchment-wide fire activity. Levoglucosan concentrations in marine sediments offshore the Amazon Estuary are positively correlated to total organic content regardless of terrestrial or marine origin, supporting the notion that association of suspended or dissolved PyC to biogenic particles is critical in the preservation of PyC. We estimate that $0.5–10 \times 10^6$ g yr^{-1} of levoglucosan is exported by the Amazon River. This represents only 0.5–10 ppm of the total exported PyC and thereby an insignificant fraction, indicating that riverine derived levoglucosan and low-temperature PyC in the tropics are almost completely degraded before deposition. Hence, we suggest caution in using levoglucosan as tracer for past fire activity in tropical settings near rivers.

Plain Language Summary During plant organic matter burning, most of the carbon is emitted to the atmosphere as CO_2, but a fraction is retained as pyrogenic biomass. The chemical composition of pyrogenic biomass depends on fire temperature and allows to differentiate between high and low-temperature pyrogenic biomass. Here, we analyzed if low-temperature pyrogenic biomass is preserved during transport in the Amazon River and deposited in western tropical Atlantic sediments. We found that only negligible amounts of low-temperature pyrogenic biomass reach the Atlantic through riverine transport. While most pyrogenic carbon (PyC) originates in the tropics, our study suggests that only an insignificant fraction of low-temperature PyC is permanently stored in marine sediments, where it would be removed from the short-term carbon cycle.

1. Introduction

Pyrogenic carbon (PyC) produced during incomplete pyrolysis of biomass constitutes an important part of the global carbon cycle (Bird et al., 2015; Jones et al., 2019; Kuhlbusch, 1998; Santín et al., 2016). PyC is directly emitted as aerosols to the atmosphere or stored in soils after fire activity. Soil PyC is transported as aerosols or by rivers in dissolved or particulate form to marine deposition areas, where it constitutes a refractory carbon pool in sediments (Coppola et al., 2018, 2019; Jaffé et al., 2013; Masiello & Druffel, 1998). PyC consists of a continuum of chemical components depending on source biomass and combustion

temperatures (Masiello, 2004). Some of the molecular components of PyC such as polycyclic aromatic hydrocarbons, produced by high temperature combustion, are not source-specific markers, as they can also be synthesized by other processes such as hydrolysis and biodegradation (Abdel-Shafy & Mansour, 2016). Conversely, the anhydro-sugar levoglucosan (1,6-anhydro-b-D-glucose) and its isomers mannosan (1,6-anhydro-b-D-mannopyranose) and galactosan (1,6-anhydro-b-D-galactopyranose) are exclusively synthesized during low-temperature (150–300°C) burning of cellulose and starch from woody and grassy biomass and their source-specific nature makes them important biomass burning tracers (Bhattarai et al., 2019; Kuo et al., 2008; Lakshmanan & Hoelscher, 1970; Simoneit et al., 1999).

Apart from widely reported atmospheric applications, there are also a few studies that used levoglucosan to trace PyC in rivers and in marine deposition areas (Hunsinger et al., 2008; Myers-Pigg et al., 2015, 2017; Schreuder et al., 2018). Since levoglucosan is preserved in sediments on geologic timescales, it has also been used to reconstruct past fire activity from marine and lacustrine sediments as well as from ice cores (dos Santos et al., 2013; Elias et al., 2001; Kawamura et al., 2012; Schreuder et al., 2019). For both applications as modern tracer and as paleo fire proxy, the understanding of the stability of levoglucosan during transport and deposition is critical. Although laboratory experiments suggest that the atmospheric lifetime of levoglucosan ranges from a few days up to one month (Bai et al., 2013; Lai et al., 2014; Pratap et al., 2019), it has been shown that levoglucosan can be preserved during long-range transport, as evidenced by its coincidence in polar ice cores with known forest fire events (Kehrwald et al., 2012). Levoglucosan is also stable in dust particles sinking through the marine water column (Schreuder et al., 2018). In rivers, levoglucosan is transported in particulate form associated to the mineral matrix as well as in dissolved form (Myers-Pigg et al., 2015, 2017). The particulate fraction directly contributes to the PyC deposited in the marine sediments, while the dissolved fraction might later contribute to the sedimentary PyC pool trough sorption to particulate organic carbon (Schreuder et al., 2018).

The riverine degradation potential of particulate levoglucosan has been studied in Arctic rivers, where levoglucosan was at least partially preserved during transport (Myers-Pigg et al., 2017). Elevated levoglucosan concentrations observed in coastal sediments at the mouth of the Santa Clara River and in the Puget Sound on the North American west coast also indicate preservation during riverine transport (Hunsinger et al., 2008; Kuo et al., 2011). Contrastingly, an incubation experiment has shown fast degradation of dissolved levoglucosan in rivers (Norwood et al., 2013) and open marine sediments from the tropical Atlantic preserve less than 5% of the direct input of levoglucosan from sinking particles (Schreuder et al., 2018). Hence, the stability of levoglucosan during riverine transport and deposition in marine sediments remains unclear, especially in the tropics and subtropics, where 90% of global PyC is produced (Jones et al., 2019).

One of the most important sources of PyC exported to the tropical ocean is the Amazon River (Coppola et al., 2018). While forest fires are a natural part of the ecosystem, slash and burn deforestation as well as an increase in drought induced wildfires have led to a further intensification of fire activity in the Amazon (Aragão et al., 2018). PyC constitutes over 10% of organic carbon in Amazonian soils and the Amazon River exports $1.09 \pm 0.218 \times 10^{12}$ g yr^{-1} particulate PyC to the ocean, accounting for 2.5%–8% of the global riverine PyC export (Coppola et al., 2018; Koele et al., 2017). The Amazon River thereby transports more than twice as much PyC than any other river, highlighting the relevance of the Amazon River system in the global PyC cycle. While high temperature PyC transport has been studied in the Amazon River and other tropical rivers, low temperature varieties have not been analyzed yet. To fill this gap in the understanding of tropical PyC transport, we study the transport and deposition of levoglucosan associated to particulate material in the Amazon River system. We analyze suspended and riverbed sediments from the Amazon main stem and from all its major tributaries as well as marine sediments from the deposition areas in and outside the modern Amazon Plume (Figure 1).

2. Environmental Setting and Methods

2.1. Study Area

The Amazon River Basin drains large parts of tropical South America and is mostly covered by tropical rainforest with restricted savanna and shrubland areas occurring mostly at the northern and southern edges of the basin (Adeney et al., 2016; Olson et al., 2001). Mean annual temperatures in the lowland Amazon
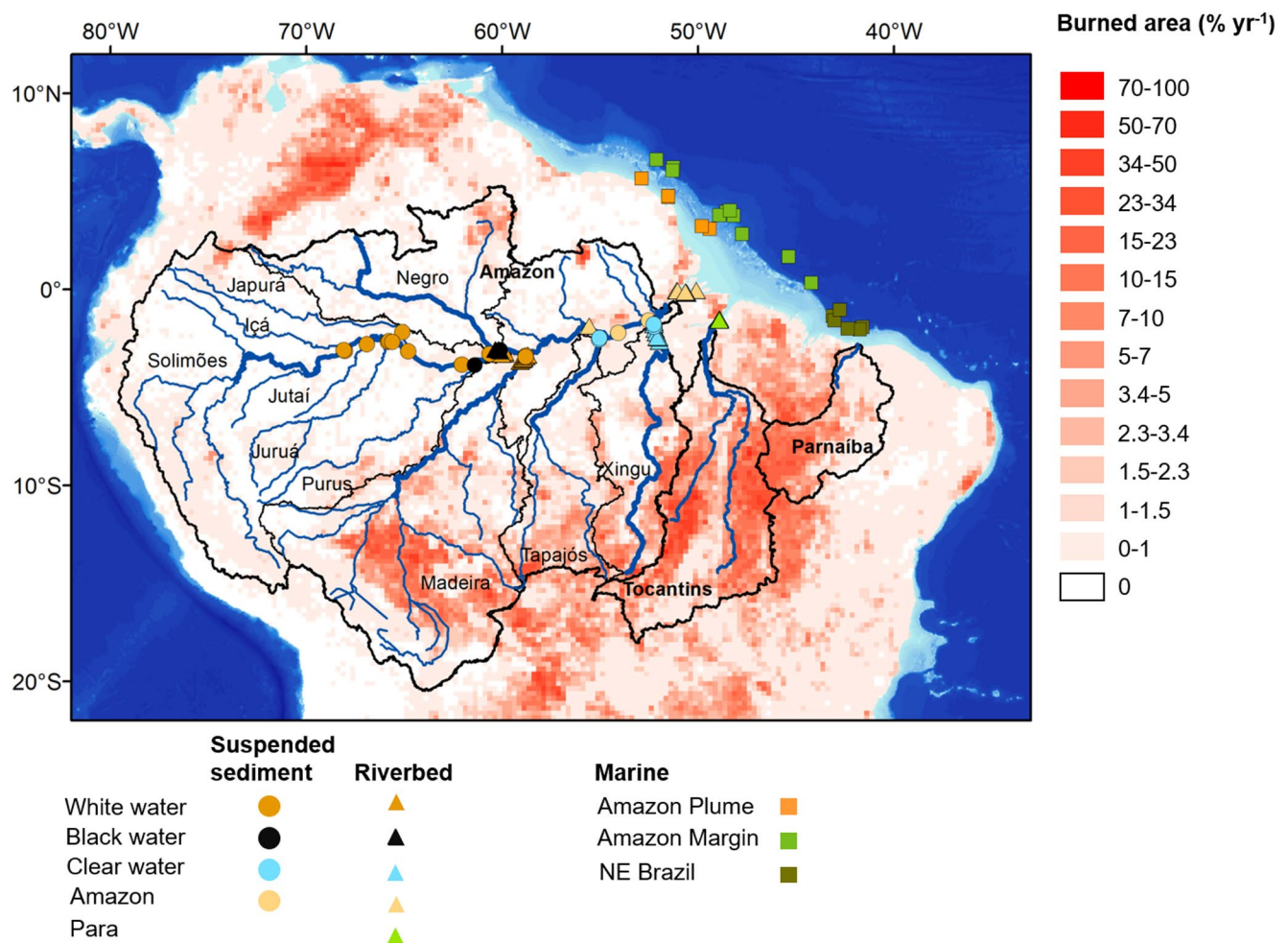
Figure 1. Map of the study area. Mean annual burned area (2003–2016) in tropical South America is depicted on a logarithmic scale from white (0%) to red (100%; Andela et al., 2019; Giglio et al., 2018). The catchment of the Amazon, Tocantins, and Parnaíba Rivers are given in thick black lines and bold labels. The catchments of the major Amazonian tributaries are given in thin black lines and standard font labels. Sample sites for suspended river sediments are given in circles, while sample sites for riverbed sediments are given in triangles. Coloring corresponds to the type of sampled tributary. Marine surface sediment sites are given in squares and coloring corresponds to the deposition sites under the Amazon Plume, at the Amazon Margin and offshore NE Brazil.

Basin range from 24 to 28°C (Fick & Hijmans, 2017). Mean annual precipitation is lowest in the eastern and southern parts with values as low as 1,500 mm yr^{-1}, while precipitation amounts of up to 3,000 mm yr^{-1} can be found in the western and northwestern parts of the basin (Fick & Hijmans, 2017). Fire activity in tropical South America is concentrated in the drier parts located in the transition zone between the Amazon Rainforest and savanna areas north and south of the Amazon Rainforest, while the central and western Amazon Basin rarely experience wildfires (Figure 1; Andela et al., 2019; Giglio et al., 2018).

The Amazon River and its tributaries drain both mountainous areas in the Andes as well as the extensive cratonic lowland. The two large Andean tributaries, the Solimões, and Madeira Rivers transport large amounts of sediment to the lowland. Due to the light brown color induced by the high suspended sediment load they are classified as whitewater rivers (Gibbs, 1967). The large lowland tributaries, the Xingu, Tapajós, and Negro Rivers, drain cratonic areas and transport smaller sediment loads (McClain & Naiman, 2008). Due to their clear waters resulting from lower concentrations of suspended sediment, the Xingu and Tapajós Rivers are classified as clearwater rivers, while the Negro River is classified as blackwater river due to its dark water color induced by the high load of dissolved organic compounds (Konhauser et al., 1994). Despite not being directly connected with the Amazon River, the Tocantins River in the southeast of the Amazon is also included in the Amazon Basin. It also drains cratonic areas and transports a low sediment load, being classified as a clearwater river. Its estuary, the Pará River, also receives Amazon River sediment

input through secondary channels influenced by tides. Due to their different sediment loads, the organic carbon concentrations found in riverine sediments vary strongly between the different tributary types and sediments transported by lowland tributaries have higher organic carbon concentrations than Andean tributaries (Häggi et al., 2016; McClain & Naiman, 2008). After discharge to the equatorial Atlantic, Amazonian water and sediments are transported northwestwards along the South American continental margin by the North Brazil Current eventually getting deposited on the continental shelf and slope all the way to the Caribbean Sea (Muller-Karger et al., 1988). Areas to the south of the Amazon Estuary and on the continental slope immediately to the east of the Amazon Estuary receive no modern sediment input by the Amazon. Rather, they are influenced by small coastal rivers and by the Parnaíba River draining semi-arid northeastern Brazil (Zhang et al., 2015).

2.2. Sampling

Riverbed sediment samples were collected using a Van Veen bottom sampler in the Amazon River and its tributaries in October 2011 (dry season) and May 2012 (wet season). Samples were taken in the Amazon Estuary as well as close to the confluence of each tributary to the Amazon main stem. Previous analysis of the samples was conducted by Häggi et al. (2016). This study found that some of the sediments in the lower Xingu River ria are derived from the Amazon River and were therefore not considered to be derived from the Xingu River in the present study. Suspended sediment samples were collected using a tangential flow filtration system during two expeditions to the Amazon River and its tributaries in September and October of 2015 (dry season). Detailed sample descriptions can be found in Data Set S1 and Häggi et al. (2019). Most samples were taken at 60% water depth to sample average conditions in terms of suspended sediment content and flow velocity (Gordon et al., 2004). Water was filtered using a Merck Millipore Ultrafiltration system equipped with Pellicon 2 Ultrafiltration cassettes coupled to a Masterflex easy load II pump head until the sample volume was condensed below 1 L. Samples were then transferred to 1-L teflon bottles and frozen. To study the deposition of PyC exported by the Amazon River to the western equatorial Atlantic, we analyzed marine surface sediments collected along the continental margin of equatorial South America that cover regions inside and outside the modern Amazon River sedimentation area. Samples were taken during *RV Maria S. Merian* cruise MSM20/3 in February and March 2012 (Mulitza et al., 2013) and during the *RV Knorr* cruise KNR/97-4 in February and March 2010 using a multi corer. Detailed sample description can be found in Data Set S1 and in Häggi et al. (2016).

2.3. Analytical Procedures

Riverbed and suspended sediment samples were freeze-dried and ground by mortar and pestle. Marine sediments and riverbed sediments were extracted in an accelerated solvent extractor (ASE) 200 ASE using dichloromethane (DCM): methanol (MeOH) 9:1 for three 5 min cycles at 100°C and 1,000 psi. Suspended sediment samples were extracted in an ASE 300 device also using DCM: MeOH 9:1 for three 5 min cycles at 100°C and 1,000 psi. The riverbed and marine extracts were dried in a Heidolph ROTOVAP system. The suspended sediment extracts were dried under a flow of nitrogen and residual water was removed over Na_2SO_4 pipette columns. Subsequently 5% splits were taken from the riverbed and marine sediment samples using DCM:MeOH 9:1 as solvent. For the suspended sediment samples 20% splits were taken. As internal quantification standard 0.5 ng deuterated (D7) levoglucosan ($C_6H_3D_7O_5$; from Cambridge Isotope Laboratories) was added to each sample. Thereafter, extracts were filtered through polytetrafluoroethylene (PTFE) filters (0.45 μm) using acetonitrile (ACN): H_2O 95:5 as solvent.

Levoglucosan and its isomers were quantified on an Agilent 1290 Infinity Ultra-high performance liquid chromatographer (UHPLC) coupled to an Agilent 6230 Time-Of-Flight (TOF) mass spectrometer following the protocol described by Schreuder et al. (2018) that adapted a previous HPLC method by Hopmans et al. (2013). Separation was achieved with two Acquity UPLC BEH amide columns (2.1 × 150 mm; 1.7 μm, Waters Chromatography) in series with a 50 mm guard column kept at 30°C. Injection volume was 10 μl for all samples. Compounds were consecutively eluted (0.2 mL/min) with ACN:H_2O 92.5:7.5 + 0.01% triethylamine (TEA) for 15 min, followed by back flushing with ACN:H_2O 70:30 + 0.01% TEA for 15 min and re-equilibration at starting conditions for 25 min. Source settings for negative ion electrospray ionization (ESI) were: Nebulizer P 60 psi (N_2), VCap 5 kV and drying gas (N_2) 5 L/min at a temperature of 275°C. The
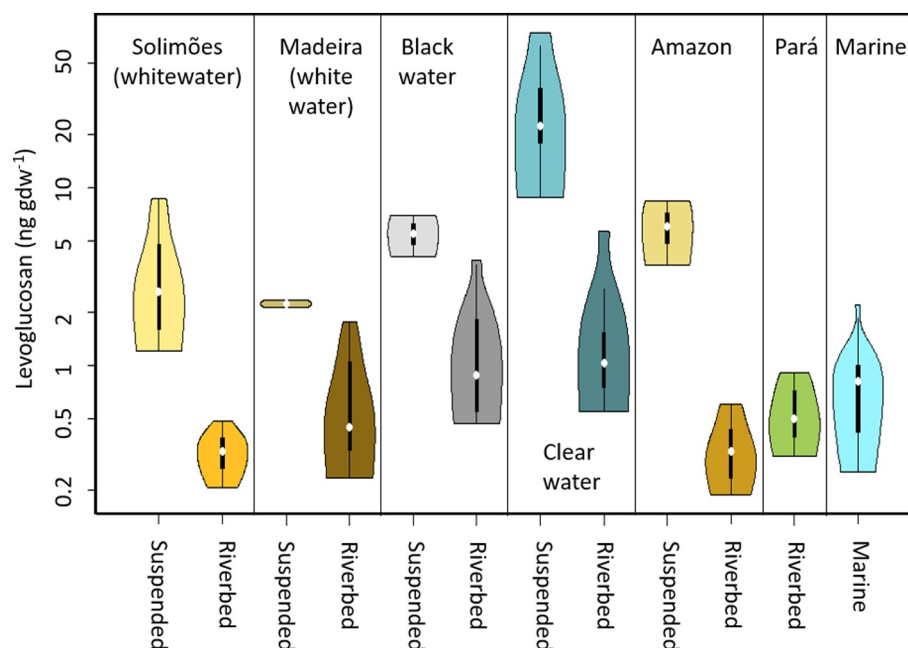
Figure 2. Violin plots of suspended sediment, riverbed sediment and marine surface sediment dry weight levoglucosan concentrations in the Amazon River and its tributaries as well as marine offshore areas. The black lines represent box-whisker plots and the white point the median. The violins represent kernel density plots that are cut off at the data limits. Blackwater river sediments consist of samples from the Negro and Purus Rivers, while clearwater samples are from the Tapajós and Xingu Rivers. Suspended sediments from the Solimões also consist of sediments from its tributaries, the Içá, Jutaí, Juruá, and Japurá Rivers. The Pará River is the name of the Tocantins Estuary.

monitored mass range was *m/z* 150–350. Levoglucosan, mannosan, galactosan and the internal deuterated levoglucosan standard were detected as their deprotonated molecules (M-H)⁻. Quantification was based on peak integrations of mass chromatograms using a calculated exact mass of *m/z* 161.0445 for levoglucosan and its isomers and *m/z* 168.0884 for the internal deuterated levoglucosan standard. The relative response was monitored daily by an external standard solution containing deuterated levoglucosan, levoglucosan, galactosan, and mannosan. Reproducibility was tested by reanalysis of 20% of the samples, yielding an average difference of 9% between replicates.

2.4. Statistical Analysis

Statistical analyses presented in this study were conducted with the statistical software R (R Core Team, 2019). We analyzed the dependence of levoglucosan on total organic carbon (TOC) content for the marine samples by performing linear regressions. To determine if mean levoglucosan concentrations from different sediment types were significantly different, the unpaired two-samples Wilcoxon test was used. This test was selected since Shapiro-Wilk tests of the data sets indicated that they do not follow a normal distribution (Table S1). The violin plots presented in Figures 2, 3 and 6 were created using the R-package vioplot (Adler & Kelly, 2019).

3. Results

Our measurements of levoglucosan and its isomers yielded quantifiable levoglucosan concentrations in all analyzed sediments. Mannosan and galactosan were below the quantification limit for most samples and we therefore focus on the results of levoglucosan analysis.

We find that the levoglucosan concentrations in suspended sediments from the Amazon River and its tributaries vary between 1.2 and 73.5 ng g⁻¹ dry weight sediment (gdw) with an interquartile range of $3.9^{+4.6}_{-1.6}$ (Q^{75}_{25}) ng gdw⁻¹ (Figure 2; Data Set S1 for raw data). The highest values ranging from 4.1 to 73.5 ng gdw⁻¹
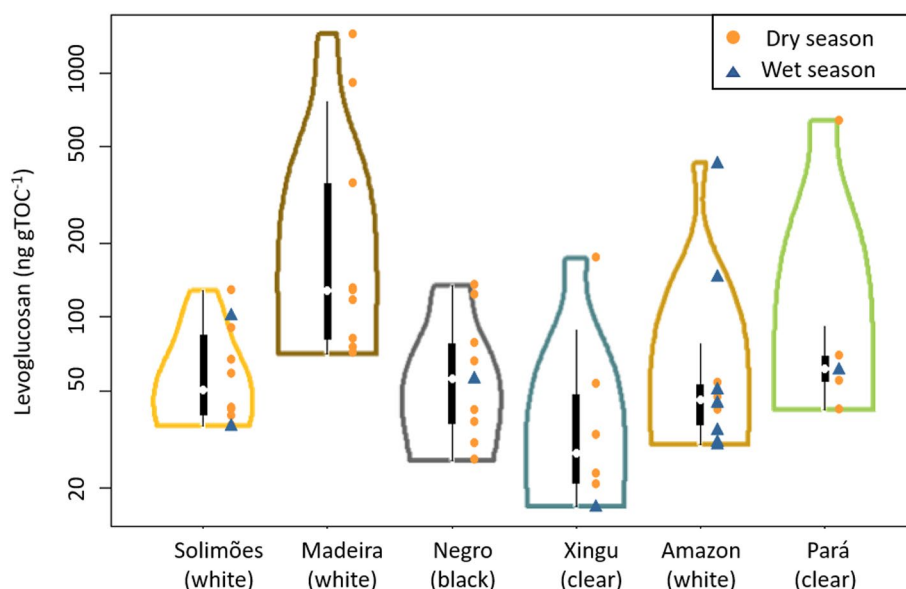
**Figure 3.** Violin plots of total organic carbon (TOC)-normalized riverbed sediment levoglucosan concentrations in the main Amazonian tributaries and the Amazon main stem. The black lines represent box-whisker plots and the white point the median. The violins represent kernel density plots that are cut off at the data limits. The individual data points are given as triangles (wet season) and points (dry season).

are found in the clear- and black water tributaries, represented by the Xingu, Tapajós, and Negro Rivers, while values in the Amazon main stem and the whitewater tributaries are markedly lower, between 1.2 and 8.7 ng gdw^{-1} (Figure 2). The levoglucosan concentrations found in riverbed sediments have values between 0.2 and 5.7 ng gdw^{-1} and an interquartile range of 0.47 $^{+0.35}_{-0.14}$ ng gdw^{-1} (Figure 2). The trend with higher values in black and clearwater rivers observed in the suspended sediment samples are paralleled by the levoglucosan concentrations from the riverbed sediments. The highest riverbed sediment levoglucosan concentrations between 0.5 and 5.7 ng gdw^{-1} are again found in the clearwater and blackwater tributaries, while the whitewater tributaries and the Amazon mainstem show lower values between 0.2 and 1.7 ng gdw^{-1} (Figure 2). The riverbed sediments from the Pará River, the estuary of the Tocantins River, also show lower values, between 0.3 and 0.9 ng gdw^{-1} (Figure 2). Overall, the riverbed levoglucosan concentrations are on average over 10 times lower and significantly different from the suspended sediment levoglucosan concentrations (Wilcoxon test, p-value $= 1.6 \times 10^{-9}$; Table S1).

Using TOC data from Häggi et al. (2016) and Sun et al. (2017), we normalized the levoglucosan concentration in the riverbed sediments to TOC-concentrations and found that the trends toward higher values in the clearwater and blackwater rivers are no longer present (Figure 3). In addition, our data also indicates that there is no systematic difference in levoglucosan concentrations between riverbed sediments collected during the wet and dry season (Figure 3).

Levoglucosan concentrations in marine sediments offshore the Amazon Estuary vary between 0.3 and 2.2 ng gdw^{-1} with an interquartile range of 0.81 $^{+0.18}_{-0.39}$ ng gdw^{-1} and thereby show comparable values to the riverbed samples with no significant difference between the mean of the two types of sediment (Wilcoxon test, p-value $= 0.08$; Figures 2 and 4; Table S1). We find a significant positive correlation between TOC and levoglucosan concentrations ($r^2 = 0.48$, $p = 0.0004$; Figure 5a). This pattern arises regardless of the terrestrial or marine origin of organic matter (Figures 5a and 5b). There are no enhanced levoglucosan concentrations in samples that have elevated terrestrial organic matter input as indicated by published BIT-index data representing the relative input of terrestrial derived versus marine organic matter (Figure 5b; Häggi et al., 2019; Hopmans et al., 2004).
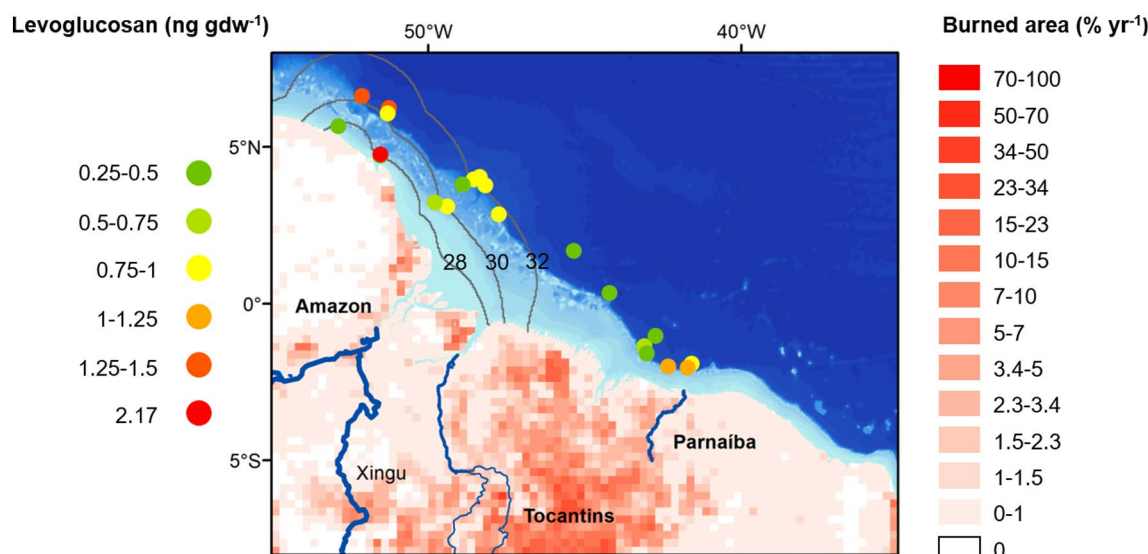
Figure 4. Map of dry weight levoglucosan concentrations in marine sediments from the western equatorial Atlantic. Note that the points indicating the positions and concentrations at sites GeoB16218-3 (2.17 ng gdw^{-1}, shown) and GeoB16220-1 (0.43 ng gdw^{-1}) completely overlap. The gray lines represent the minimal surface salinity during the annual cycle indicating the extent of the Amazon Plume (Sbrocco & Barber, 2013). Mean annual burned area data is shown as in Figure 1 (Andela et al., 2019; Giglio et al., 2018).

4. Discussion

4.1. Riverine Transport of Levoglucosan

4.1.1. Regional Variability

Both suspended and riverbed sediments show the highest levoglucosan concentrations in the clearwater and blackwater tributaries that carry a typically lower sediment load than whitewater tributaries, but higher organic carbon concentrations. The higher TOC concentrations in the clearwater and blackwater river
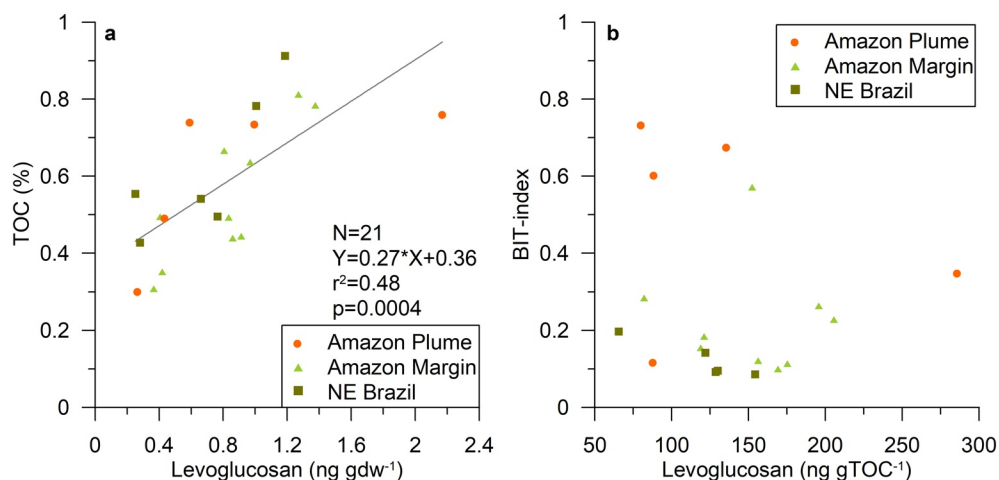
Figure 5. Relationship of marine surface sediment levoglucosan concentrations and total organic carbon (TOC) content of samples collected from the western equatorial Atlantic. (a) Regression between levoglucosan concentrations and TOC concentrations from Häggi et al. (2016) and Sun et al. (2017). If the data point with the highest levoglucosan concentration is treated as an outlier (see also Figure 4 for comparison) the regression is improved ($r^2 = 0.57$; $p = 0.0001$). (b) Relationship between TOC-normalized levoglucosan concentrations and the BIT-index representing the relative input of terrestrial organic matter (the higher the BIT-index value, the larger the fraction of terrestrial organic matter in TOC) from Häggi et al. (2019). The panel illustrates that the contribution of terrestrial organic matter input does not influence levoglucosan concentrations.
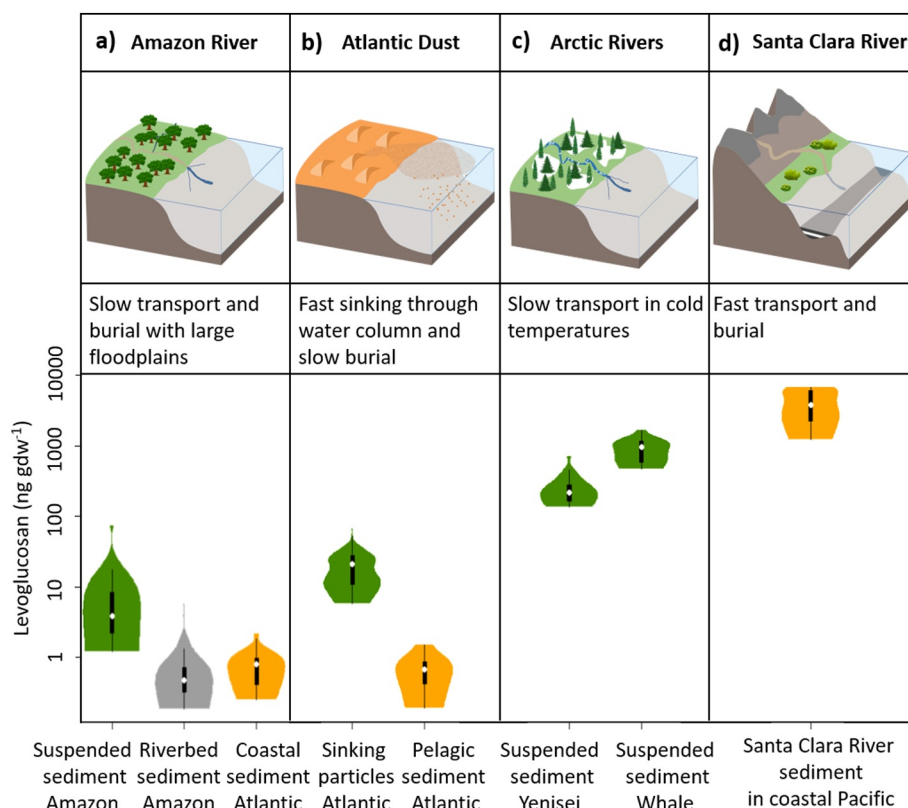
Figure 6. Comparison of levoglucosan transport in the Amazon River to other transport and deposition modes. (a) Amazon River transport; (b) dust transport into the tropical Atlantic Ocean (Schreuder et al., 2018); (c) suspended sediments from the Arctic Yenisei and Great Whale Rivers (Myers-Pigg et al., 2017); (d) marine sediments derived from the mountainous Santa Clara River in Southern California (Hunsinger et al., 2008).

sediments partly explain this pattern since TOC-normalized values do not show this trend (Figure 3). From the fire activity data shown in Figure 1 (Andela et al., 2019; Giglio et al., 2018), one would expect to see elevated levoglucosan levels in the clearwater rivers (i.e., Tocantins, Xingu, and Tapajós), in the Madeira River and in marine sediments near the Parnaíba River if there was a relation between levoglucosan yield and fire activity. Conversely, the Solimões River and Negro River basins feature lower fire activity and would thereby be expected to have lower levoglucosan yields. Yet, both the dry weight and TOC-normalized concentrations show no geographical distribution that fits to the fire pattern (Figures 2 and 3). The Xingu River, for instance, has the lowest TOC-normalized values despite high fire activity in its catchment (Figure 3), while the Negro River has some of the highest dry weight sediment concentrations despite low fire activity in its basin (Figure 2). Thus, our results suggest that there is no relation of riverbed and suspended sediment levoglucosan concentrations with recent fire activity in each tributary catchment. Given that all different catchments are mostly covered by rainforest vegetation, it is also unlikely that the different tributaries have contrasting abundance of high or low temperature fire activity that would explain the observed pattern.

4.1.2. Riverine Transport of Levoglucosan

In aerosols from the Amazon rainforest levoglucosan constitutes up to 8% of TOC in smoke samples and can also constitute a substantial fraction of TOC in samples that are not directly impacted by fire (Claeys et al., 2010; de Oliveira Alves et al., 2015; Graham et al., 2003; Kundu et al., 2010; Schkolnik et al., 2005). This indicates that levoglucosan initially forms a substantial fraction of PyC produced in the Amazon Basin. In riverbed sediments from the Amazon River and its tributaries, we find that levoglucosan only represents 0.02–1.5 ppm of TOC (Figure 3), even though PyC in sediments from the lower Amazon River has been found to make up 10% of TOC (Coppola et al., 2018). Levoglucosan can rapidly degrade in aerosols and during soil incorporation (e.g., Knicker et al., 2013; Lai et al., 2014). Moreover, the erosion from soils and

sediments lowers the particulate levoglucosan concentrations by dissolution of levoglucosan not associated to the soil matrix, which is then transported in dissolved form (Myers-Pigg et al., 2015, 2017). The eroded suspended sediment is thereby already depleted in levoglucosan compared to soils.

Our results also provide evidence that further degradation occurs during fluvial transport. First, our results show a consistent decrease of levoglucosan concentrations from suspended sediments to riverbed sediments within all studied tributaries and the Amazon main stem (Figure 2). Riverbed sediments have by trend a coarser grain size than suspended sediments and thereby a lower organic content, which would have the potential to explain some of the discrepancies between the suspended sediment and riverbed concentrations. However, the riverbed samples analyzed in this study come from different parts of the river channel both covering coarse-rained (sand) and fine-grained (mud) sediments with TOC values up to 7% that include the grain size fraction represented in suspended sediments. Therefore, the riverbed samples analyzed in this study have overlapping grainsize distributions and TOC-contents with suspended sediments from the Amazon River system (Häggi et al., 2016). This indicates that the difference in levoglucosan concentrations between the suspended sediment and riverbed samples of on average one order of magnitude is likely not exclusively caused by differences in grain-size composition. An alternative explanation relates to the different sampling times of the suspended and riverbed samples. Myers-Pigg et al. (2017) showed variations in particulate levoglucosan transport in the Yenisei and Great Whale Rivers depending on the sampling season. In the Amazon River, however, seasonality is much less pronounced than in Arctic rivers (Callède et al., 2004). Moreover, our riverbed sediments were sampled during the wet and dry seasons and do not show any systematic difference between them (Figure 3). Part of the difference between suspended sediment and riverbed samples is likely caused by an enhanced degree of degradation in riverbed sediments compared to suspended sediments. Riverbed sediments are transported slower than suspended sediments (Gordon et al., 2004) allowing for longer degradation. A fast decomposition of levoglucosan is supported by the observation from incubation and laboratory experiments showing that levoglucosan in both soils and aerosols can be degraded within days under exposure to high oxygen and temperature conditions (Knicker et al., 2013; Lai et al., 2014).

Second, levoglucosan concentrations in riverine sediments are also lower than in lacustrine sediments from the neotropics that are less prone to remineralization of organic carbon than Amazonian river sediments. Lacustrine sediments from small lake catchments already experienced transport and leeching by dissolution but transport time and distance are limited, and deposition environments are often anoxic or suboxic favoring levoglucosan preservation. A lacustrine levoglucosan sediment record from the eastern Amazon shows distinct TOC variability with values between 2% and 7% in the lower part of the sediment core, while the upper part has values >40% (Elias et al., 2001). In the lower part, where TOC values are comparable to our riverbed samples, with values of 0.1%–7% (Häggi et al., 2016), levoglucosan concentrations vary between 100 and 900 ng gdw^{-1} (Elias et al., 2001). Another neotropical lacustrine record from Guatemala shows values between 10 and 100 ng gdw^{-1} for sediments with TOC contents between 0.8% and 10% (Schupbach et al., 2015) that are also comparable to the ones found in Amazonian riverbed sediments from our study. This comparison illustrates that neotropical lacustrine levoglucosan concentrations are higher than those found in both Amazonian suspended (3.9$^{+4.6}_{-1.6}$ ng gdw^{-1}) and riverbed (0.47 $^{+0.35}_{-0.14}$ ng gdw^{-1}) sediments, often by more than an order of magnitude, suggesting that levoglucosan in suspended sediments in the Amazon River represent a degraded signal even compared to other tropical sediments. Furthermore, levoglucosan concentrations in Amazonian River sediments show similar concentrations to open marine sediments from the central tropical Atlantic, which are degraded and preserve less than 5% of the levoglucosan concentrations yields found in sinking particles (Figure 6; Schreuder et al., 2018). This further supports the notion that levoglucosan concentrations in the Amazon River represent a degraded signal.

Organic matter is recycled in the extensive floodplains of the Amazon, which could lead to further degradation of organic matter derived from upland forest (*terra firme*) soils where most of the fire activity takes place (Richey et al., 2002). Indeed, pollen data from the Amazonian tributaries shows that *terra firme* forest derived organic matter is sometimes masked by floodplain-derived material (Akabane et al., 2020). Moreover, our suspended sediments were collected close to the confluence of each tributary with the Amazon main stem (Figure 1), where they already experienced long transport and degradation. While our study indicates that levoglucosan concentrations in riverine sediments represent a degraded signal, it does not

allow for the quantification of degradation during the different stages of production, storage, and transport. To fully understand the cycling of levoglucosan and low-temperature PyC in the Amazon Basin, further source-to-sink studies would be needed that focus on how much of the high levoglucosan yields produced in fires are preserved in soils or directly transported to rivers via aerosols. Furthermore, it would be necessary to systematically study transfer and dissolution effects during soil storage and erosion (Marques et al., 2017). During transport, the establishment of annual or multiannual timeseries of levoglucosan concentrations in sediments from selected stations would be useful to account for seasonality and the impact of specific fire events (Myers-Pigg et al., 2017).

One note of caution in comparing levoglucosan abundances is that extraction protocols sometimes vary between studies. Comparative studies on soils and aerosols have shown that the most commonly used extraction protocol for levoglucosan using MeOH or DCM:MeOH mixtures yielded comparable result (Cordell et al., 2014; Hopmans et al., 2013). While these comparisons were conducted on modern sample material, a study from a Pleistocene marine sediment core showed that MeOH extraction was on average five times more efficient than DCM:MeOH 9:1 (Ruan et al., 2020). While all modern marine and riverine sediment data sets reported here were produced using DCM: MeOH mixtures, the discussed Holocene lacustrine sediment records were produced using MeOH as extraction solvent (Elias et al., 2001; Hunsinger et al., 2008; Myers-Pigg et al., 2017; Schreuder et al., 2018; Schupbach et al., 2015). Thereby, all other modern data sets discussed in this study have been obtained using a similar methodology than used in this study and the data from the sediment records used for comparison were extracted with the preferable methodology for these types of samples. Given that concentrations between different deposition settings vary by sometimes several orders of magnitude (Figure 6), we argue that the impact of varying extraction efficiencies of different solvents on reported levoglucosan concentrations is not large enough to impact our findings.

4.2. Marine Deposition of Levoglucosan

The levoglucosan distribution in western tropical Atlantic surface sediments does not show different values for samples collected in areas under the modern influence of Amazonian river sedimentation and samples collected in areas without contribution of Amazonian sediments (Figures 4, 5a and 5b). This finding contrasts with the otherwise strong difference in organic matter provenance and composition observed in sediments from in- and outside the influence of the Amazon Plume (Häggi et al., 2015, 2016, 2019; Sun et al., 2017). There is also no increase in levoglucosan concentrations in samples from NE Brazil offshore the Parnaíba River that drains shrubland (Caatinga) areas with high modern fire activity (Figure 4). Rather, levoglucosan concentrations in the studied marine sediments are related to TOC-content regardless of the proportion of aquatic and terrestrial derived organic matter (assessed by the BIT-index) and geographic distribution (Figures 5a and 5b). This indicates that levoglucosan concentrations in the western tropical Atlantic represent a preservation signal with higher levoglucosan yields preserved in sediments with higher TOC-content and are not related to the degree of riverine terrestrial input.

Previous studies on PyC have found that suspended particulate PyC as well as dissolved PyC can sorb onto sinking particulate organic matter and thereby get preserved in sediments (Coppola et al., 2014). In sinking particles in the tropical Atlantic, levoglucosan was also found to be associated with biogenic particles rather than mineral dust particles (Schreuder et al., 2018). This could explain why the levoglucosan concentrations under the influence of the Amazon Plume are comparable to areas that receive almost exclusively marine organic matter input (Figure 4). Interestingly, the preservation of levoglucosan in sediments deposited under the influence of the Amazon Plume, where sediment accumulation rates are in the range of cm yr^{-1} (Kuehl et al., 1986), is similar than preservation in sediments from the Amazon margin and offshore NE-Brazil, where sediment accumulation is in the range of cm kyr^{-1} or even features no modern sedimentation (Zhang et al., 2015). This suggests that the small portion of levoglucosan closely associated to biogenic particles may evade degradation, even under conditions favoring degradation. We also find that the levoglucosan concentrations in our coastal marine sediments ($0.81\,^{+0.18}_{-0.39}$ ng gdw^{-1}) are comparable with riverbed sediments ($0.47\,^{+0.35}_{-0.14}$ ng gdw) and marine sediments along a transect across the tropical Atlantic Ocean ($0.68\,^{+0.19}_{-0.15}$ ng gdw^{-1}; Figure 6; Schreuder et al., 2018). This further indicates that there is a small refractory portion of levoglucosan associated to particulate organic carbon that seems to be relatively constant across the Atlantic and stable to further degradation. Overall, the analysis of marine surface sediments indicates

that the most important factor controlling levoglucosan content is preservation regardless of marine or terrestrial organic matter provenance (Figure 5a). The proportion of direct sourcing of particulate levoglucosan from the Amazon River is likely highest in the Amazon Plume. The regions that receive mostly marine organic carbon input have likely a higher proportion of previously dissolved and suspended levoglucosan adsorbed to sinking biogenic particles. This fraction is likely dominantly derived from biomass burning aerosol input that is mostly derived from Africa in the western tropical Atlantic (Barkley et al., 2019; Prospero et al., 2020).

4.3. Implications

4.3.1. Comparison to PyC Flux

The marine and riverbed sediment levoglucosan concentrations can be used to estimate the net export of levoglucosan by the Amazon River and compare it to PyC flux estimates. Coppola et al. (2018) used riverbed sediments from the lower Amazon to estimate PyC fluxes. They found that PyC represents $10.0 \pm 1.7\%$ of TOC. They then upscaled their measurements to the total particulate organic carbon export by the Amazon of 1.08×10^{13} g y^{-1} (Galy et al., 2015) to arrive at an annual PyC flux of $1.09 \pm 0.218 \times 10^{12}$ g yr^{-1}. Following the same approach, we find that levoglucosan represents $46\,^{+7}_{-9}$ ppb of TOC in samples from the Amazon Estuary (Figure 3). Thereby, levoglucosan represents only ca. 0.5 ppm of PyC exported by the Amazon River, which stands in strong contrast to the high levoglucosan yields found in modern wildfires, where levoglucosan constitutes up to 8% of TOC (de Oliveira Alves et al., 2015). Applying the upscaling approach of Coppola et al. (2018) would indicate that the levoglucosan export by the Amazon River is 5×10^5 g yr^{-1}. While most of the samples in our data set show relative stable values as represented by the interquartile range of $46\,^{+7}_{-9}$ ppb, there are two samples, where levoglucosan represents 127 and 429 ppb of TOC, leading to a considerable discrepancy between the median value of 46 ppb in Amazon Estuary sediments and the average of 90 ppb (Figure 3). In general, the samples with the highest TOC normalized levoglucosan yield are low TOC samples that have a reduced contribution to the total TOC flux. As we find consistently higher levoglucosan concentrations in the suspended sediments than in riverbed sediments (Figure 2), the overall export is likely higher than the estimate based on riverbed sediments. Suspended sediments from the lower Amazon River yielded 3.7 and 8.4 ng gdw^{-1}. Given the annual export of 1.1–1.3×10^{15} g of sediment to the tropical Atlantic (Meade et al., 1985), this would indicate an export of 4–11×10^6 g yr^{-1} based on the suspended sediment yields alone. Combining the results from the riverbed and suspended sediments we, therefore, estimate a total levoglucosan export by the Amazon River to be between 0.5 and 10×10^6 g yr^{-1}.

Given the potential addition of dissolved levoglucosan by adsorption to biogenic particles and the discrepancy of sinking particles and surface sediment levoglucosan yields observed in other marine sediments (Schreuder et al., 2018), exported levoglucosan in particulate sediment is not a conclusive measure to assess the amount of levoglucosan that is eventually deposited in marine sedimentation areas. Overall, levoglucosan deposition is fundamentally linked to TOC deposition in the submerged Amazon Delta and the shelf areas along the coast of northern South America, independently of origin or local sediment accumulation rate (Figure 5a). Increased marine productivity may therefore also lead to enhanced levoglucosan deposition. Since levoglucosan concentrations in marine sediments are closer to the values found in riverbed sediments than to suspended sediments (Figure 6), the export estimate based on riverbed sediments is likely more accurate in assessing the eventual deposition of levoglucosan.

4.3.2. Comparison to Other Rivers and Deposition Areas

Our findings suggest that levoglucosan, and thereby low-temperature PyC, is almost completely degraded before reaching marine deposition areas. This contrasts findings from sediments in high latitude rivers as well as from the small mountainous Santa Clara River in California (Figure 6; Hunsinger et al., 2008; Myers-Pigg et al., 2017). Suspended sediments from the Arctic Yenisei River yield $225\,^{+65}_{-55}$ ng gdw^{-1} particulate levoglucosan, while the Great Whale River in Québec yields $990\,^{+200}_{-380}$ ng gdw^{-1} (Myers-Pigg et al., 2017) and thereby concentrations that are two orders of magnitude higher than the $3.9\,^{+4.6}_{-1.6}$ ng gdw^{-1} found in the suspended sediments of the Amazon River and its tributaries (Figure 6). Marine sediments collected offshore the mouth of the Santa Clara River in Southern California contain $3920\,^{+2430}_{-1620}$ ng gdw^{-1} levoglucosan and thereby three to four orders of magnitude more than sediments in areas offshore the Amazon Estuary,

despite similar TOC-concentrations of 0.1%–2.2% (Figure 6; Hunsinger et al., 2008). In deposition areas across the Atlantic, sinking particle concentrations of $21.4^{+6.9}_{-10.3}$ ng gdw^{-1} are degraded to $0.68^{+0.19}_{-0.15}$ ng gdw^{-1} during deposition at the sediment surface (Figure 6; Schreuder et al., 2018).

Overall, the comparison to other rivers and marine deposition areas suggest that fast transport and deposition is critical for preserving levoglucosan in sediments. This leads to the maximal levoglucosan concentrations at the Santa Clara River mouth as source-to-sink transport in the Santa Clara River takes place during storm events and may take only hours to days and the source areas are prone to high wildfire activity (Marlon et al., 2012; Warrick et al., 2015). Apart from the impact of transport and deposition velocity, large lowland rivers in the Arctic also transport greater amounts of levoglucosan than the Amazon River (Figure 6; Myers-Pigg et al., 2017). This may be caused by lower air and water temperatures, which have found to be important in the preservation of levoglucosan in aerosols (Bai et al., 2013) and generally decrease degradation rates of organic matter (Arndt et al., 2013). It is therefore likely that high temperatures are also responsible for the strong degradation of levoglucosan in tropical lowland rivers on top of long transport times. Moreover, the transfer of PyC in the Amazon River might be further impeded by large floodplains that separate the rivers from terra firme forests where most of the fires occur (Hess et al., 2015; Sanford et al., 1985).

4.3.3. Low-Temperature PyC Cycling in the Tropics

In combination with previous results by Schreuder et al. (2018), our results suggest that low-temperature PyC is mostly degraded during both riverine transport and dust transport to the Atlantic Ocean and only a small fraction of levoglucosan is deposited in offshore areas (Figure 6). Thus, low-temperature PyC does not form a significant portion of permanent carbon burial in the tropical Atlantic. This is of special relevance since 90% of global PyC is produced in tropical and subtropical savannas and rainforests (Jones et al., 2019). The strong degradation of low-temperature PyC contrasts with the refractory behavior of high temperature PyC, where tropical rivers such as the Amazon and the Congo Rivers export higher yields than any other rivers in the world (Coppola et al., 2018). Our results also indicate that levoglucosan deposition in marine environments is not necessarily related to direct terrestrial input. In contrast, our marine sediment data suggest that adsorption of dissolved PyC to biogenic particles resulting from marine productivity might be of key importance in controlling the deposited levoglucosan concentrations. This results in a pattern where levoglucosan concentrations across the tropical Atlantic are within the same order of magnitude regardless of provenance (Figure 6).

4.3.4. Reconstruction of Past Fire Activity

The strong degradation of levoglucosan in the Amazon River has also implications for its use as proxy for past fire activity. Our study shows that fire activity is only one variable among many that can influence the export of levoglucosan to sedimentary archives. Degradation during transport and sedimentation in marine areas can also have a major impact on levoglucosan concentrations. All these factors need to be considered when inferring paleo fire changes from levoglucosan concentrations in riverine sediments deposited in marine environments. Since there is so far no measure to assess the degree of degradation of levoglucosan (i.e., by comparing with another sugar that shows similar degradation rates), it is yet not possible quantify to what degree degradation controls variations in sediment records. In the case of the Amazon River, major changes in sediment transport dynamics and shifts in marine deposition areas during the past 50,000 years, thereby, present a major challenge to perform paleo fire reconstructions based on levoglucosan (Häggi et al., 2017, 2019; Pupim et al., 2019; Wang et al., 2017).

5. Conclusions

We studied the transport of the low-temperature biomass burning tracer levoglucosan in suspended and riverbed sediments from the Amazon River system and its deposition in marine surface sediments from the western tropical Atlantic. We found that a major fraction of levoglucosan adsorbed to particles is degraded during riverine transport or trapped by the extensive floodplains bounding the Amazon River, restricting input to river channels. Therefore, there is no relationship between levoglucosan concentrations in riverine sediments and fire occurrence in the catchments of the Amazonian tributaries. There is a small fraction of

$0.5–10 \times 10^6$ g yr^{-1} particulate levoglucosan exported by the Amazon River and deposited in the tropical Atlantic, that only accounts for 0.5–10 ppm of the total PyC exported by the Amazon (Coppola et al., 2018). Levoglucosan concentrations in marine sediments are comparable to riverbed sediments from the Amazon River system and show no geographic pattern associated with the modern Amazon Plume. Rather, the levoglucosan concentrations are related to TOC-content, regardless of the proportion of terrestrial and aquatic TOC. This suggests that sorption of dissolved levoglucosan to particulate organic carbon may present an additional process to direct particulate input to sediments. The degradation complicates the use of levoglucosan as a fire tracer in the Amazon Basin. Overall, our study shows that riverine input of levoglucosan and low-temperature PyC to the tropical Atlantic negligible, even though the tropics are responsible for 90% of PyC production. This suggests that low-temperature PyC is not a relevant fraction in the long-term burial of carbon in marine sediments in the tropics.

Data Availability Statement

All data are available in Data Set S1 and archived on www.pangaea.de (Häggi et al., 2021; https://doi.org/10.1594/PANGAEA.931789).

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