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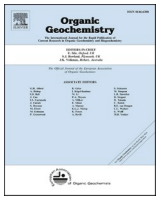

Quantification and isotopic characterization of benzene polycarboxylic acids (BPCA)-derived black carbon in deep oceanic sediments: Towards assessing pyrogenic inputs from marine sources

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ABSTRACT

Methodologies based on benzene polycarboxylic acids (BPCA) selectively target the polymeric aromatic fraction of black carbon (BC) and are considered adequate to quantify pyrogenic inputs in environmental samples such as soils, lakes, and marine dissolved organic carbon. However, the usefulness of these methodologies to quantify BPCA-derived BC in deep-sea sediments has not been fully evaluated. In this manuscript we describe and validate a procedure to quantify BPCAs in deep oceanic sediments with very low organic carbon content. The resulting analytical procedure has produced reproducible quantitative data for BPCAs over a period of 10 months (coefficient of variation, CV = 6.4 − 6.6%). The stable carbon isotopes ($\delta^{13}C$) of BC_BPCA have been characterized using an LC Isolink™-irMS system with an accuracy better than 0.5‰. The quantitative and isotopic composition of several marine sediments has been characterized to investigate the relative contributions of marine/diagenetic and continental/pyrogenic sources to the BC accumulated in oceanic sediments from different contexts, ranging from upwelling systems to remote oceanic locations. Overall, a significant fraction of the sedimentary BC is of marine origin and should be considered in inventories of pyrogenic materials accumulated in the world oceans. However, the continental/pyrogenic sources can be largely dominant in marine settings with large inputs of pyrogenic materials.

1. Introduction

Black carbon (BC) has been the subject of numerous biogeochemical and paleoclimatic studies to trace the fate of pyrogenic carbon (PyrC) in the environment (Vaezzadeh et al., 2021; Coppola et al., 2022; Mekonnen et al., 2022; Wöstehoff et al., 2022). The BC designation encompasses a broad spectrum of materials, exhibiting varying chemical compositions and structures, commonly linked to organic substances derived from pyrogenic processes (Hedges et al., 2000; Masiello, 2004). As a consequence, inconsistent results are given when comparing different BC methodologies since each one targets a specific BC / PyrC fraction (Schmidt et al., 2001; Brodowski et al., 2005; Hammes et al., 2007; de la Rosa et al., 2011; Schneider et al., 2011; Hanke et al., 2017; Zimmerman and Mitra, 2017).

Benzene polycarboxylic acids (BPCAs) are specific molecular markers used to quantify and characterize the polycondensed aromatic fraction of BC / PyrC (Glaser et al., 1998; Wiedemeier et al., 2015; Hindersmann and Achten, 2017), termed BC_BPCA to avoid confusion with other methodologies (Zimmerman and Mitra, 2017). This technique relies on the oxidation of BC with nitric acid to convert the condensed aromatic fraction of BC to 8 small molecules that can be separated and quantitated individually (Suppl. Fig. 1). The total abundance of all BPCA homologues provides information on the fate of the polycondensed aromatic fraction in environmental samples (Schneider et al., 2010; Ziolkowski et al., 2011; Wiedemeier et al., 2015; Wagner et al., 2017; Kappenberg et al., 2019). Also, the relative concentrations of the 3, 4, 5, and 6 substituted BPCA compounds offer information on the chemical composition of the condensed polyaromatic fraction. A high proportion of B6CA has been related to highly condensed BC formed at high temperatures (Schneider et al., 2010; Wiedemeier et al., 2015; Kappenberg et al., 2019) or to highly transformed fossil organic materials, such as coal and petroleum (Hindersmann and Achten, 2017).

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BPCA methodology has been successfully used to assess the BC_BPCA presence and composition in soils (Czimczik et al., 2003), coastal sediments (de la Rosa et al., 2011; Sánchez-García et al., 2013) and dissolved organic matter (DOM) (Dittmar, 2008; Stubbins et al., 2012; Ding et al., 2013; Wagner et al., 2017). However, the utility of BC_BPCA to investigate the sources and distribution of BC / PyrC in the world oceanic sediments is still to be exploited (Coppola et al., 2014).

The analytical protocol initially proposed by Glaser et al. (1998) is laborious and involves many procedural steps including a pre-digestion to remove polyvalent cations, a nitric acid (HNO_3) oxidation of the condensed polyaromatic structures to generate BPCA compounds, an elimination of poly-charged cations with column chromatography, and a compound derivatization prior to GC-FID detection. A number of modifications to the original protocol of (Glaser et al., 1998) have been proposed over the last 20 years to reduce the analytical load associated with BPCAs quantitation (Brodowski et al., 2005; Schneider et al., 2011; Wiedemeier et al., 2013; Hindersmann and Achten, 2017). With liquid chromatography (LC) implementation as a detection technique (Dittmar, 2008; Schneider et al., 2011), the processing time required for BC analysis was reduced as derivatization was not necessary. However, quantitative values produced with GC and LC may not be comparable due to systematic differences among methodologies. This study aims at improving the analytical outcomes associated with BPCA-derived BC in deep sea sediments using LC-UV detection. Also, it includes an evaluation of the pyrogenic and non-pyrogenic sources of BC_BPCAs in marine sediments derived from the $\delta^{13}C$ composition of the TOC and the BC_BPCA fraction. The specific goals of this report are to: 1) minimize the procedural burden to increase sample throughput, 2) evaluate the analytical performance of all procedural steps, 3) demonstrate the method's applicability in remote oceanic sediments, 4) validate the resulting analytical protocol and define the long-term analytical reproducibility, 5) characterize the $\delta^{13}C$ value of BC with accuracy useful for environmental studies, and 6) evaluate the relative contributions of marine and continental/pyrogenic contributions to the BC_BPCA accumulated in deep-sea sediments.

2. Materials and methods

2.1. Samples and standards

Standards of mellitic acid (B6CA, ref. M2705), pyromellitic acid (1,2,4,5-B4CA, ref. B4007), trimellitic acid (1,2,4-B3CA, ref. B4589) and trimesic acid (1,3,5-B3CA, ref. 482749) were obtained from Sigma-Aldrich. The benzene pentacarboxylic acid (B5CA) standard was purchased at TCI (ref. B0952). Marine Sediment (NIST Standard SRM 1941b) was used to evaluate analytical accuracy. Samples of char and soot were gathered to optimize microwave temperature and digestion time settings. These samples were obtained by burning oak wood in a household cast iron stove. The tar sample consisted of the condensed materials accumulated in the stove exhaust at the end of the winter season. The char sample was retrieved from the ashes. The temperature and duration of combustion for these materials were not controlled.

A deep sea control sample was produced by mixing a number of sediments collected across the central Atlantic Ocean (2020, R.V. Endeavour cruise EN651, 3000 – 4000 m below surface). Three sediment cores (30–50 cm long) were retrieved using a multicorer device (ST5 at 5.003287°N, 33.613422°E; ST6 at 4.991015°N, 30.061943°E; ST7 at 5.162817°N, 27.000593°E) and the bottom 5–10 cm of each core were combined to obtain approximately 1–1.5 kg of wet sediments. This sediment sample was freeze-dried and homogenised and was used for method development and to assess the analytical reproducibility.

2.2. Analytical procedure

2.2.1. Microwave acid digestion and filtration

Approximately 300 mg of marine sediment were placed in a 55 ml MARSXpress (CEM Corp.) vessel and oxidised with 5 ml of 67 – 69% HNO_3 (trace metal grade, Fisher Scientific, Leicestershire, UK) for 6 h at 160 °C in a MARS 6 microwave (CEM Corp.). The digestion method increased the temperature to 160 °C in 10 min and then it was held for 6 h. After sample oxidation, 20 ml of Milli-Q water were added to each sample to dilute the HNO_3 before filtration. The diluted digest was transferred to a 10 ml glass syringe equipped with a 15 mm diameter glass-fiber filter. Sample transfer was completed with additional volumes of Milli-Q water (2 x 2.5 ml). The combined extract was filtered with vacuum assistance. The resulting HNO_3-containing solution was evaporated using a MARS6 XpressVap evaporation system (CEM Corp.) during 50 min to a final volume of approximately 1 ml.

2.2.2. Sample purification

Polyvalent cations were removed chromatographically using a cation exchange resin (Dowex 50Wx8, 200—400 mesh, Sigma Aldrich, USA). The resin (20 g) was suspended in Milli-Q water and loaded onto a glass column (250 mm long, 30 mm inner diameter, Vidrafoc, Spain) equipped with a grass frit (porosity P0). The resin was conditioned to obtain the H^+ form with: (1) 20 ml of Milli-Q water, (2) 60 ml of 2.4 M NaOH, (3) 40 ml of Milli-Q water, (4) 80 ml of 2 M HCl and (5) 80 ml of Milli-Q water. The process of column conditioning was accelerated with the assistance of a mild pressure at the top of the column. Each column could be used for multiple samples, and the conditioning process was applied between samples to remove retained polycations.

Extracts in concentrated nitric acid (1 ml) were diluted with 9 ml of Milli-Q water and loaded onto the column. BPCAs were eluted with 60 ml of 40% methanol (MeOH). Purified extracts were concentrated using the MARS6 XpressVap system (CEM Corp.) during 50–60 min to a final volume of 1 ml approximately. The extracts were transferred into 10 ml glass tubes and evaporated to dryness under N_2 stream at 90 °C. Samples were redissolved in 0.5 ml of 1% phosphoric acid (Sigma-Aldrich, ref. W290017) in Milli-Q water (LC phase A) and transferred into a 2 ml glass vial prior to LC-UV analysis.

2.2.3. LC-UV analysis

BPCAs were analysed using a high-performance liquid chromatography (HPLC) system consisting of a quaternary pump (P680, Dionex, Thermo Scientific), an automatic sample injector (ASI-100, Dionex, Thermo Scientific), and a diode array detector (UltiMate 3000, Dionex, Thermo Scientific). The LC column used was an Agilent Poroshell 120 SB-C18 column (3 × 100 mm, 2.7 μm). Compounds were eluted using a solvent gradient from 100% A to 30% A in 10 min followed by isocratic conditions during 2 min. The column was conditioned during 7 min with 100% A between sample analysis. Solvent A was obtained by diluting 1.1 ml of 85 % phosphoric acid with 0.5 L of Milli-Q water. Solvent B was acetonitrile (HPLC-grade, Merck). BPCA detection and quantification was performed by comparing their absorbance at 240 nm with standard solutions using an external linear calibration curve with a dynamic range of 0.5 to 100 μg / ml. For each BPCA, a linear curve was adjusted using the minimum squared regression method for instrumental calibration. Thermo Chromeleon 7.2 SR4 software was used for data acquisition and processing.

2.2.4. LC Isolink™-irMS

High performance liquid chromatography-stable carbon isotope ratio mass spectrometry of B5CA and B6CA was achieved using a modification of the methodology proposed by (Wagner et al., 2017). The HPLC system used was a Dionex Ulitimate 3000 (Thermo Fisher Scientific) equipped with a quaternary pump, automatic injector, column oven, and a diode array UV–Visible detector. Adequate separation of B5CA and B6CA was performed using an Agilent Poroshell 120 ODS column (3 × 150 mm, 2.7 μm) held at 13 °C. The composition of elution solvent A was 3% phosphoric acid. Solvent B was obtained by dissolving 2.42 g NaH_2PO_4-monohydrate (Merck) and 0.42 g Na_2HPO_4-heptahydrate (Merck) in 1 l of Milli-Q water. Mobile phases were sonicated

under vacuum for 5 min prior to use. Due to the global He scarcity, we refrained from using the continuous He flush typically recommended by the manufacturer. No significant increase in the CO_2 background signal was observed over 5 days. BPCA compounds were eluted at a flow rate of 0.3 ml / min using a gradient from 0% B to 100% B in 20 min, followed by isocratic elution at 100% B during 31 min.

Since lipidic compounds may be difficult to elute from a reverse phase column using water-based solvents, we removed the apolar compounds from the sample extracts with a C18 cartridge (3 ml, Supelco, ref 52603-U). Extracts were loaded onto the cartridge and the unretained BPCAs were eluted with 3.5 ml of Milli-Q water to ensure complete recovery (Wagner et al., 2017). Both loading and elution solvents were combined and evaporated to dryness. Samples were redissolved with 500 μL of 3% phosphoric acid.

The online conversion of BPCAs to CO_2 was achieved using a LC Isolink™ interface (Thermo). The LC mobile phase was mixed with 60 μl / min of 300 g / l phosphoric acid and 60 μl / min of sodium persulphate (300 g / l). The resulting mixture was heated at 99.9 °C to oxidize any organic material eluting from the LC column. The produced CO_2 was recovered using an in-line membrane permeable to CO_2 and transported to the irMS system using a flow of He (ca. 1 ml / min). The He carrier gas was dried using Nafion membranes to minimize the input of water to the irMS system. Typical background levels of CO_2 produced by the HPLC Isolink™ system ranged between 100 and 200 mV (m / z 44, cup 2) and stable $\delta^{13}C$ measures could be observed whenever the O_2 background in the irMS remained between 10 and 40 V (m / z 32, cup 2).

Data were analysed with Isodat software (version 2.5; Thermo Fisher Scientific). All analyte peaks were manually integrated to ensure that the $\delta^{13}C$ values were calculated accurately. The long-term accuracy and reproducibility of the system was continuously controlled by bracketing the same standard mix containing B5CA and B6CA every five or six analytical runs. The LC Isolink™-irMS setup produced $\delta^{13}C$ measurements with an accuracy and reproducibility better than 0.5‰.

To ensure that reported $\delta^{13}C$ measurements are traceable to international standards we characterized the isotopic composition of commercially available B6CA and B5CA compounds using a Flash Elemental Analyzer connected to an irMS (Delta V Advantage, Thermo Scientific) using an Conflo IV interface. The isotopic values provided by the EA-irMS system were calibrated with international standards (IAEA-600 and IAEA-C8). Measured $\delta^{13}C$ values for B5CA and B6CA standards were −27.46‰ (N = 6, s = 0.01) and –23.83‰ (N = 6, s = 0,03), respectively. These values were used to characterize the $\delta^{13}C$ composition of the CO_2 reference gas of the LC-Isolink-irMS system. Several pulses of calibrated CO_2 were incorporated during each LC-Isolink-irMS run to ensure the traceability of reported $\delta^{13}C$ values to the international standards described above.

2.2.5. Data collection, analysis, and processing

The statistical data analysis for this paper was generated using the Real Statistics Resource Pack software (Release 8.9.1). Copyright (2013 – 2023) Charles Zaiontz. www.real-statistics.com. Graphs were obtained using the Excel software (Microsoft Corp.) and linear regressions were performed using the weighted least squared method with a weighting factor of 1 / Y.

Maps were created using the QGIS software, v 3.30, https://qgis.org/). Data of global surface chlorophyll were retrieved from the Giovani website (Aqua MODIS Global Mapped Chlorophyll Data, version R2022.0 https://doi.org/10.5067/AQUA/MODIS/L3M/CHL/2022, accessed 08/03/2023). Data on pyrogenic carbon emissions were retrieved from https://daac.ornl.gov/VEGETATION/guides/fire_emissions_v4_R1 (accessed July 2023, Randersson et al., 2017).

3. Results and discussion

3.1. Sample pre-treatment with TFA

Accurate BPCA quantitation requires a complete removal of polycharged cationic species from the sediment digest. In neutral or alkaline solution, BPCAs polymerize spontaneously and rapidly with polycharged cations, such as Al^{3+}, Ca^{2+}, and Fe^{3+}, to produce stable polymers (Loiseau et al., 2006). Therefore, sediment digests much be kept in strongly acidic conditions until polycations are quantitatively removed from solution. To minimize the risk of BPCA sequestering by polycations, (Glaser et al., 1998) included a pre-digestion step with hydrochloric acid (HCl) prior to the nitric oxidation of BC. However, this procedural step has proven controversial. (Brodowski et al., 2005) detected artefactual BPCA formation during HCl pre-digestion and replaced it with trifluoroacetic acid (TFA). However, a number of authors described BPCA losses associated with sample handling during the TFA pre-digestion process (Ziolkowski and Druffel, 2009; Schneider et al., 2011; Wiedemeier et al., 2013), specifically during sample filtration to remove the metal-rich TFA solution. Accordingly, this step is often omitted in spite of the risk of inadequate polycation removal (Glaser et al., 2021). We have investigated the effect of TFA predigestion by comparing the quantitative values with and without TFA pre-treatment in soot and char samples. The applied protocol was a variation of the method described by Brodowski et al., (2005) and consisted of a microwave-assisted (MA) digestion (25 min, 100 °C) in a TFA solution (4 M), followed by extract filtration to remove the extracted cations. We visually observed that char and soot particles stick to the glassware during sample handling (i.e., filtering, extracts transfer), and significant losses of BPCA were observed in almost all experiments (soot 20.7 ± 12.7 and char 19.5 ± 11.1%, N = 8, Suppl. Table 1). Accordingly, the TFA pre-treatment was discarded and the cation removal in marine sediments depends entirely on the cation-exchange resin performed after HNO_3 digestion.

3.2. Optimization of microwave-assisted digestion

We have optimized the experimental conditions (temperature and digestion time) to maximize the amount of BPCAs released from char and soot samples through a MA digestion. Recoveries of B6CA and B5CA were temperature dependent, and maximum recoveries were obtained at 160 – 170 °C (Fig. 1). Optimal digestion times ranged between 4 and 6 h for soot and char samples, respectively. B3CA and B4CA recoveries decreased at longer digestion times, suggesting BPCAs degradation during sample digestion.

Degradation of individual BPCAs during nitric digestion was further studied by treating solutions containing 5 BPCA standard compounds (B6CA, B5CA, 1,2,4,5-B4CA, 1,3,5-B3CA, and 1,2,4-B3CA) with nitric acid at different digestion temperatures (140 – 170 °C). Other experimental conditions, such as digestion times (6 h), BPCA addition (200 μg for each compound), and volume of nitric acid (5 ml) remained constant. Loss of mass was calculated by comparing HPLC peak areas between processed and unprocessed standard solutions, and expressed in terms of mass degraded per digestion time (μg / h). As detailed in Fig. 2, degradation rates of individual BPCAs during MA digestion increased linearly with the different applied temperatures. Losses were compound-dependent and ranged from 2.7 μg for B5CA to 12.6 μg for 1,2,4-B3CA, assuming a digestion process of 6 h at 160 °C (Table 1). In general, highly substituted compounds (B6CA and B5CA) were significantly more stable than B3CA and B4CA. BPCAs losses during digestion represented less than 6.3% of the added standard compounds. Additional tests performed in the 20 – 200 μg range resulted in total recoveries higher than 80%. However, recoveries decreased to 50 – 90% at low

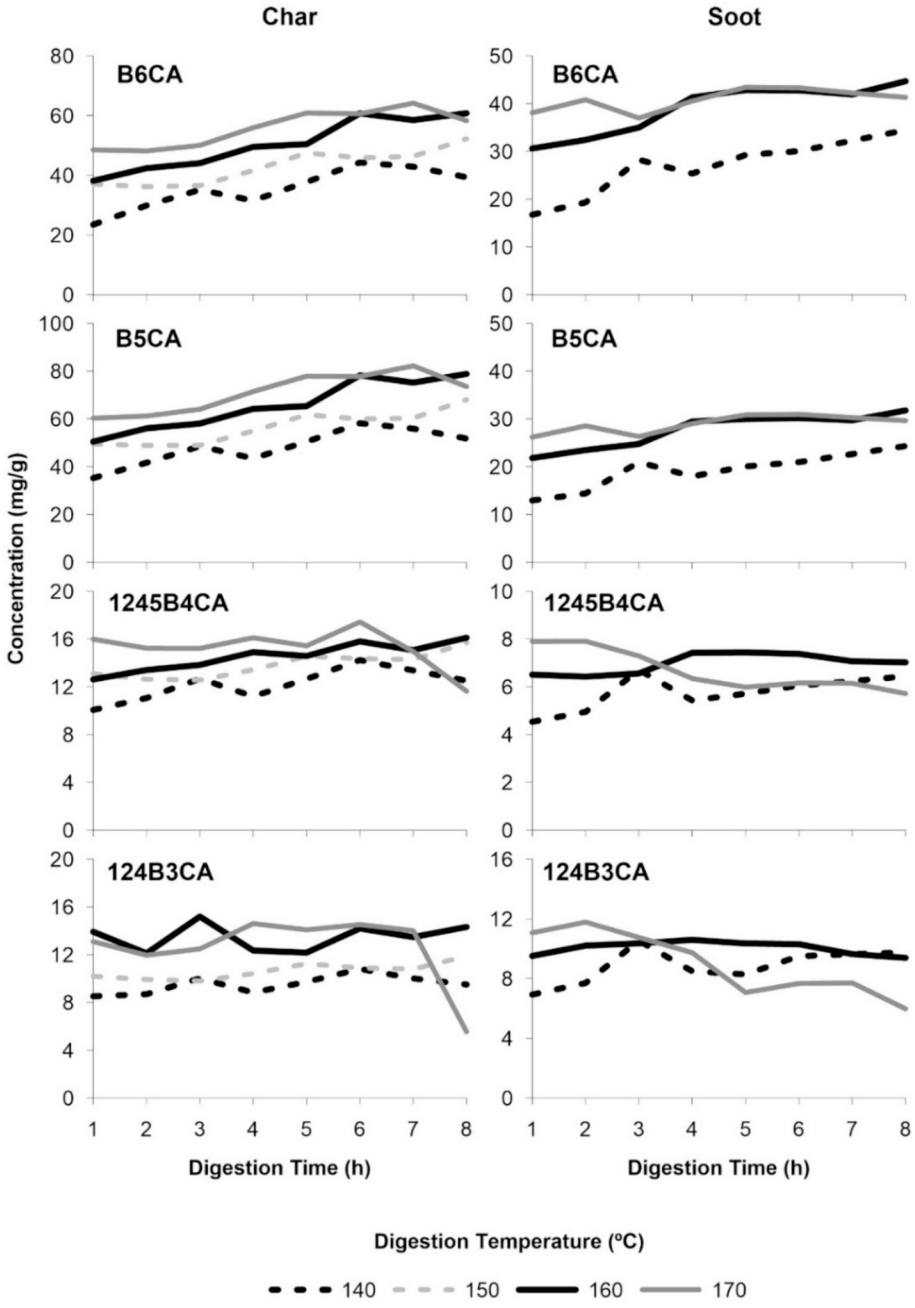

Fig. 1. Microwave-assisted digestion of char and soot samples. Concentration of BPCAs recovered at different temperatures and digestion times.

BPCAs concentration values (1 – 20 μg added, data not shown). Overall, sample losses during microwave digestion were comparable to reported losses in experiments with oven-heating at 170 °C over 8 h (Dittmar, 2008; Ziolkowski et al., 2011; Wiedemeier et al., 2013; Glaser et al., 2021), and do not involve a major change in the accuracy of BPCA-derived BC estimates.

To investigate the influence of microwave activation on the kinetics of BC decomposition in nitric acid, we have compared the amount of BPCA released with and without microwave activation at different time periods. Soot and char samples were digested during variable time periods (1 — 8 h) using a microwave system at 160 °C and were compared with the results obtained with a regular oven set at 170 °C. BPCA produced with and without MA assistance was not different (Suppl. Fig. 2). Most of the BPCAs were produced within the first 60 min of digestion (ca 65% for soot and 80 — 90% for char), and the digestion proceeded at a slower pace during the following 5 — 7 h. Remarkably, BC degradation occurred at slower pace in the MA experiment, indicating that implementation of microwave systems does not accelerate BPCA production. The conclusion is that the results obtained using MA or oven digestion are not significantly different (Suppl. Fig. 2).

3.3. Polyvalent cation removal

The analytical reliability relies on the exhaustive removal of polycations present in the sample digest using ion-exchange column chromatography. Preliminary tests with different column dimensions and cation exchange resins (Chelex, 200–400 mesh, Bio-Rad, USA) lead to the conclusion of an optimum column size of 30 × 250 mm and a Dowex resin amount of 20 g. However, recoveries of B3CA and B4CA compounds using water as eluent were incomplete or required very high elution volumes (>150 ml per sample) that proved difficult to evaporate. Adequate recoveries (>90%) and low elution volumes (<60 ml)

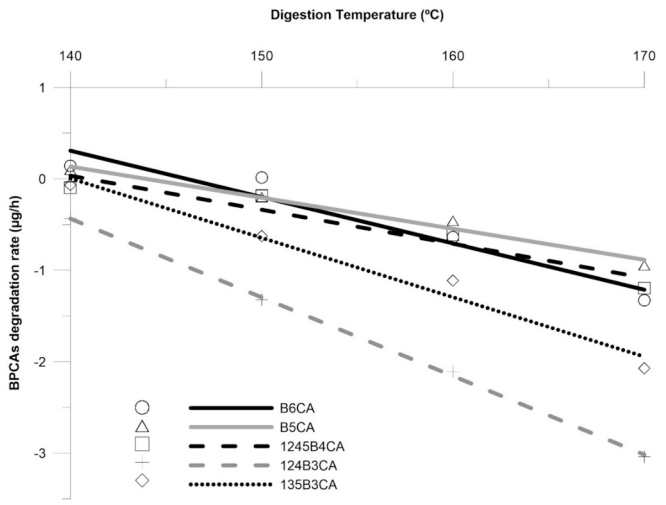

Fig. 2. Relationship between degradation rate of BPCAs (in µg/h) and temperatures. Each value is the average of duplicated experiments.

Table 1
Measured losses of BPCA standard compounds (in µg) after 6 h of microwave-assisted digestion at different temperatures (°C).

	B6CA	B5CA	1,2,4,5-B4CA	1,2,4-B3CA	1,3,5-B3CA	∑BPCAs
170	−8.0	−5.7	−7.2	−18.2	−12.4	−51.5
160	−3.8	−2.7	−3.7	−12.6	−6.7	−29.6
150	0.1*	−1.2	−1.1	−7.9	−3.8	−14.0
140	0.9*	0.6*	−0.6	−2.6	−0.4	−3.6

*Losses not considered.

Table 2
BPCA standard recoveries (%) eluted with different solvents (A-Water, B-20% MeOH, and C-40% MeOH) at different elution volumes (ml).

	Elution Volume (ml)	B6CA	B5CA	1,2,4,5-B4CA	1,2,4-B3CA	1,3,5-B3CA
A	0–20	44	31	4	0	0
	20–40	48	63	70	26	0
	40–60	2	4	21	47	3
	60–80	0	1	5	21	11
	80–100	0	0	1	6	21
B	0–20	40	33	11	2	0
	20–40	50	57	67	44	3
	40–60	4	6	23	50	28
	60–80	0	1	2	6	42
	80–100	0	0	0	1	25
C	0–20	61	53	31	22	19
	20–40	34	44	66	67	41
	40–60	1	2	4	7	30
	60–80	1	1	1	1	5
	80–100	0	0	1	1	2

were achieved with 4:6 MeOH:water (Table 2).

The capacity of ion exchange columns to retain polycations relies on high affinity to poly-charged cations, compared to mono-charged cations such as protons. However, the retention capacity of these resins is compromised when high concentrations of nitric acid are added when loading the sample digest. To increase the efficiency of the ion exchange column we evaporated the excess of nitric acid to a final volume of approximately 1 ml using an XpressVap evaporation system. This process highly improved the stability and efficiency of the ion exchange columns, while ensuring the stability of the sample extracts. Long-term experience demonstrated that the ion exchange columns provided adequate cation removal for at least six digests of 300 mg of carbonate-rich marine sediments.

3.4. Validation of the analytical setup for marine sediments

To ensure data comparability, it is necessary to implement adequate controls to demonstrate that the analytical setup produces reproducible and accurate results. Typically, the analytical accuracy is determined using reference materials of known concentration, and number of reference materials have been proposed to estimate the BC content of soils and air particulates (Hammes et al., 2007; Schneider et al., 2011). Tests performed with the reference sample NIST Marine Sediment Standard SRM 1941b produced quantitative results (9.25 ± 0.14 mg BPCA / g TOC, N = 3) similar to those previously reported using HPLC detection (9.88 ± 0.26 mg BC / g sediment, Vaezzadeh et al., 2021; 10.7 mg/g, Ziolkowski et al., 2011; ~10 mg BPCA / g TOC, Wiedemeier et al., 2013). These values are significantly higher than the ones produced using gas chromatographic detection of the trimethylsilyl-derivatives of BPCA compounds (4–40 mg/g, Wiedemeier et al., 2013). The conclusion is that quantitative values produced using microwave-assisted digestion are similar to previous studies based on LC-UV detection.

The analytical reliability of BPCA quantitation requires the implementation of adequate quality control (QC) samples in every analytical batch. Therefore, we produced one "in house" QC sediment to ensure the long-term comparability of the results produced in the laboratory (Fig. 3). This QC sample was selected to mimic the sediment composition of Atlantic sediments that contain high concentrations of interfering polycations ($CaCO_3$ > 50%, aluminosilicates > 40%) and a very low organic carbon content (TOC = 0.05 — 2%). The analytical uncertainty for B5CA and B6CA in the QC sample over 10 months was 6.4% and 6.6% respectively, and deviations from the mean value were smaller than 15% in all tests. Therefore, as a conservative estimate, the long-term analytical reproducibility was better than 10% for B5CA and B6CA. In contrast, B4CA and B3CA compounds existed in very low concentrations in marine sediments, and several interfering signals caused significant biases and uncertainties during peak identification and integration. The conclusion is that the analytical reproducibility required for environmental and paleoclimatic studies is only met for B6CA and B5CA quantitation..

3.5. Isotopic analysis of B6CA and B5CA

The LC Isolink™ system (Thermo Scientific) allows the online determination of $\delta^{13}C$ of individual compounds eluting from a liquid

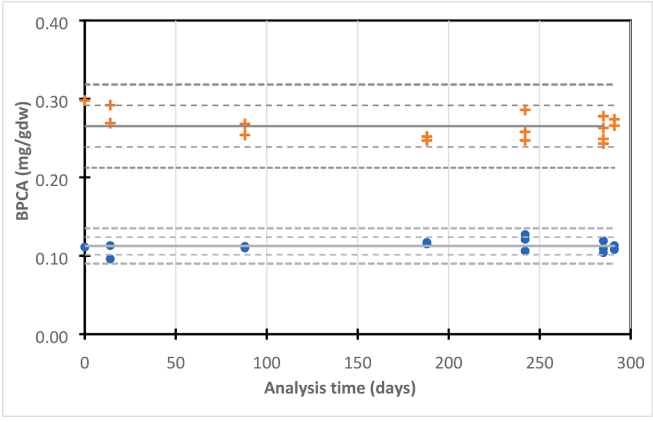

Fig. 3. Validation of the analytical method. Reproducibility of the QC samples used over a period of 10 months. The averaged concentration values are is represented with continuous lines. Dashed lines mark the position of 10% and 20% error from the mean value. Most quantitative values obtained for B6CA (crosses), and B5CA (dots), fall within ± 10% of the averaged value.

chromatographic column. This system is incompatible with LC mobile phases that contain organic solvents and requires the use of water based HPLC solvents. BPCAs were eluted using phosphate buffered at a pH value higher than the dissociation constant of B4CA and B3CA compounds (pH approximately 4.2). Under these conditions, the affinity of BPCAs to the C18 stationary phase is highly reduced and their elution from the column is achieved in less than 30 min (Wagner et al., 2017). In addition, separation of the B6CA from the solvent front could be significantly improved by increasing the concentration of phosphoric acid in the mobile phase to 3%, and by reducing the column temperature to 13 °C. This modification solved coelution issues of B6CA with unretained compounds that compromised the isotopic measurement for this compound. Tests at temperatures below 13 °C resulted in severe buildup of system back pressure, possibly caused by the accumulation of phosphoric acid in the chromatographic column. The resulting chromatographic separation ensured adequate separation from interfering compounds present in the extracts from deep sea sediments (Fig. 4) and was adequate for the isotopic characterization of B5CA and B6CA compounds. The isotopic characterization of B4CA and B3CA compounds was complicated by the coelution of interfering compounds in the chromatographic profile. In practice, this limitation was considered not relevant because B3CA and B4CA compounds were in trace amounts in all marine sediment samples analysed.

The commercial LC Isolink™ interface proved impractical and extremely expensive due to the constant clogging of the reactor. This clogging occurred within 10—14 days of continuous flow of the effluent resulting from the combination of the chromatographic mobile phase and the oxidation reagents. This issue caused the occasional blockage and breakdown of the CO_2 exchange membrane located downstream. Both issues combined were the cause of a significant increase in the cost associated with each analytical determination. We partially solved the issue by substituting the metallic tubing (and furnace) by a fused-silica tubing of similar dimensions placed into a gas chromatography oven programmed at 100 °C. The clogging issue also occurs with the fused-silica tubing, but the exchange of this part is affordable and was implemented in a regular basis to avoid the issues described above. The trade-off to this improvement is a small increase in the chromatographic peak width. However, the signal intensity, accuracy, and reproducibility of the modified LC Isolink™ configuration is comparable to the original system (Fig. 5).

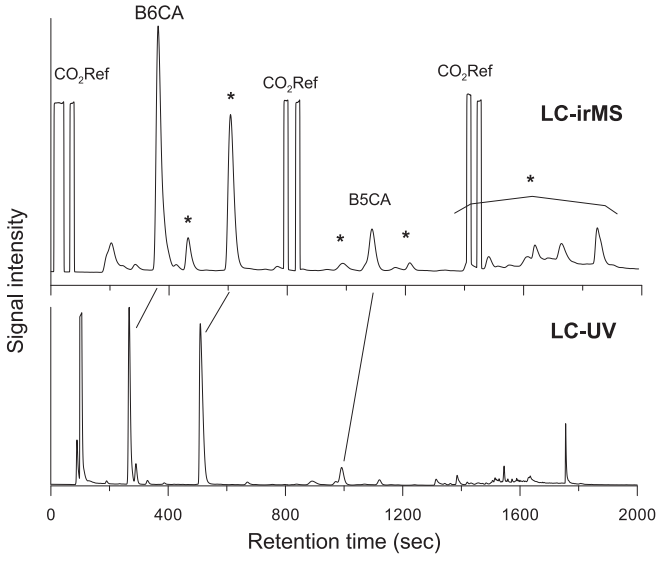

Fig. 4. LC-UV and LC-Isolink-irMS profiles corresponding to sediment sample EN651-ST04 (tropical Atlantic Ocean). Asterisks correspond to unidentified compounds. Note the significant peak broadening caused by the LC-Isolink interface.

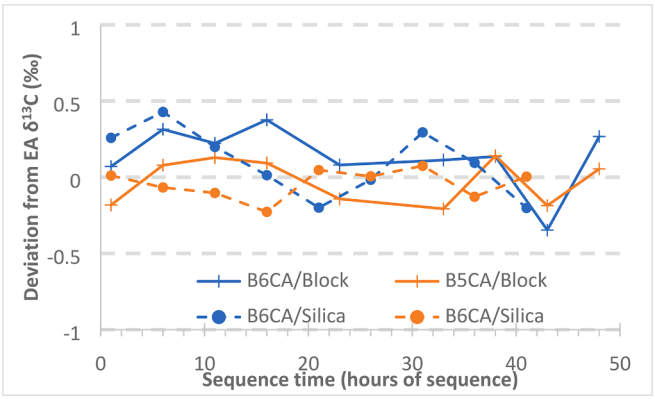

Fig. 5. Stability of two different LC-Isolink-irMS setups. Accuracy and reproducibility obtained with the standard and modified configurations (reaction block vs silica tubing) was the same for both B6CA and B5CA. Deviations from the nominal value remain systematically below 0.5‰ during a 2-days-long analytical run.

Testing with standard compounds proved that the HPLC-LC Isolink™-irMS analytical setup produced $\delta^{13}C$ measurements with an accuracy and precision better than 0.5‰ within the concentration in the range of 20 to 1000 ng of injected compound (Suppl. Fig. 3). The long-term analytical accuracy was ensured by implementing routine control standards in all analytical runs. As shown in Fig. 5, the LC Isolink™-irMS can provide stable $\delta^{13}C$ values when applied to 2 days-long analytical runs. Also, replicated analysis of the internal sediment control sample produced averaged values of -17.9 ± 0.6‰ and -18.7 ± 0.8‰ (N = 5) for B6CA and B5CA, respectively. Accordingly, this analytical setup can produce estimates of $\delta^{13}C$ with a reproducibility better than 0.8‰. In practice, the analytical $\delta^{13}C$ accuracy can be threatened by spurious coeluting compounds that may remain undetected in the relatively broad LC-irMS-derived chromatographic peak. Therefore, accuracy strongly relies on the careful manual integration to detect and remove possible interferences and/or deviations in the background signal. The occasional existence of interfering compounds can be confirmed and removed by modifying the column temperature and investigating the manifestation of shoulders in the chromatographic signal that produce significant isotopic biases. Also, duplicate analysis of sediment extracts should produce results with a difference smaller than 0.6‰. Analysis in duplicate of each extract performed on different days are also of use to detect potential interferences and/or biases in the isotope measures.

A second potential source of error in the isotopic characterization of BC is possible isotopic fractionation produced during sample preparation (nitric acid digestion, acid evaporation, cation removal, solvent evaporation, and extract cleanup). However, $\delta^{13}C$ values obtained for processed standard mixtures were not significatively different (difference < 0.32‰, N = 3) from the original isotopic value. The conclusion is that BPCA losses during sample processing, including losses during acid digestion, do not encompass any measurable isotopic fractionation for both B5CA and B6CA.

3.6. BC_BPCA in marine sediments

As described in Table 3 and Fig. 6, all analysed sediments from the Atlantic, Indian, Antarctic, and Pacific Oceans contained considerable quantities of BC_BPCA (0.033 – 0.57 mg / gdw). The highest values were obtained in organic-rich sediments underlying high productivity upwelling areas off Namibia and Peru. The lowest values corresponded to sites located far from the continents and with low surface productivity in the Atlantic and Pacific gyres. There is a strong linear relationship between the BC_BPCA and TOC measured in marine sediments (OC-BPCA = 0.00455 × TOC + 0.0293; N = 8; $R^2 = 0.84$, 1/Y weighted regression, Fig. 7 A).

Table 3
Concentration and $\delta^{13}C$ values for TOC and BPCA compounds accumulated in marine sediments.

	Latitude (°N)	Longitude (°E)	Distance to continent (km)	B6CA (mg/gdw)	B5CA (mg/gdw)	OC-B6 + 5CA (mg/gdw)	TOC (mg/gdw)	B5CA/B6CA	$\delta^{13}C$_B6CA (‰)	$\delta^{13}C$_B5CA (‰)	$\delta^{13}C$_TOC (‰)
South Atlantic1	−5.78	−10.75	1173	0.058	0.018	0.033	1.8	0.32	−19.9	−21.6	−20.2
North Atlantic	19.75	−20.78	472	0.055	0.032	0.037	4.3	0.58	−16.3	−18.1	−21.5
Tropical Pacific	11.03	−140.09	3500	0.062	0.025	0.037	4.6	0.41	−18.9	−18.4	−21.4
Tropical Indian	5.07	73.78	509	0.144	0.057	0.086	5.6	0.40	−18.4	−20.3	−19.9
Off Australia	−16.63	146.30	57	0.057	0.056	0.049	5.6	0.98	−15.5	–	−19.3
South Atlantic2	−10.12	8.01	562	0.244	0.169	0.178	8.9	0.70	−16.3	−16.5	−20.4
Upwelling Namibia	−21.10	11.82	196	0.310	0.237	0.236	46.0	0.76	−18.5	−20.6	−20.6
Upwelling Peru	−11.07	−78.08	46	0.630	0.546	0.507	108.1	0.87	–23.1	–23.7	−21.5

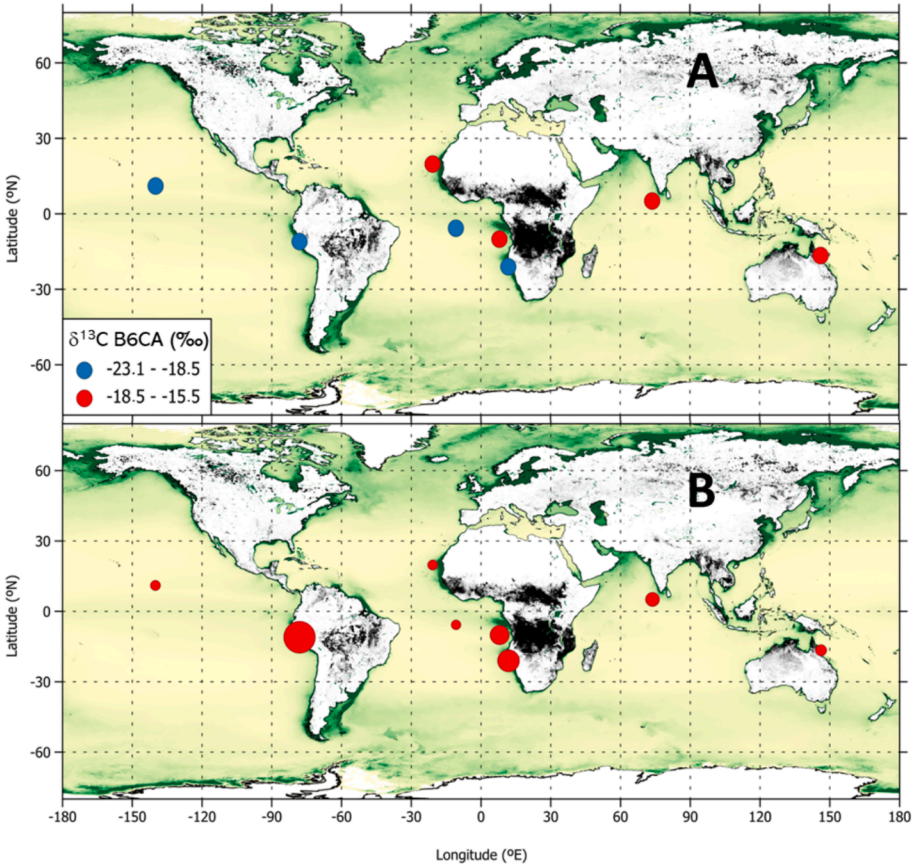

Fig. 6. Maps showing the position of the sediment samples including the $\delta^{13}C$-B6CA isotopic values (A) and OC-B5 + 6CA content (B). The size of symbols in B are indicative to the sedimentary content on OC-B5 + 6CA. In A, the $\delta^{13}C$_B6CA values less negative than −18.5‰ (red dots) indicate dominance C4-PyrC sources in the sedimentary BC. The BC_B6CA isotopic signal in sediments underlying high productivity area or from locations distant from continental masses (blue dots) is consistent with a marine origin. Black carbon emissions from wildfires (from Randersson et al., 2017) have been depicted in grey areas to highlight that tropical regions are the primary contributors to global BC emissions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The ratio B5CA to B6CA can provide information on the chemical characteristics of BC in the environment. Reduced B5CA / B6CA ratios have been related to a higher degree of condensation of the polymeric aromatic fraction associated with higher temperature of pyrolysis or higher degree of maturation of transformed organic materials (Ziolkowski et al., 2011; Wiedemeier et al., 2015; Hindersmann and Achten, 2017; Kappenberg et al., 2019). However, this ratio is susceptible to alteration in aquatic environments due to dissolution or degradation of the less condensed fraction (Bostick et al., 2018). We measured large differences in the B5CA / B6CA ratios (0.32−0.98) revealing significant differences in the BC composition in different sedimentary settings. Statistical analysis showed a low degree of covariation between the B5CA / B6CA ratio and other chemical parameters such as $\delta^{13}C$_TOC, $\delta^{13}C$_B5CA, $\delta^{13}C$_B6CA, TOC, and OC_B5 + 6CA content ($0.01 < R^2 < 0.27$). In contrast, a strong correlation was obtained with the distance of the sampling site to the nearest continental mass (B5CA / B6CA = –0.144 × Ln(Distance) + 1.47, $R^2 = 0.76$) and sediment depth (B5CA / B6CA = –0.153 × Ln(Depth) + 1.77; $R^2 = 0.64$). This correlation indicates that BC_BPCA accumulated in remote and deep locations is depleted in the less condensed and most labile fraction, resulting in low B5CA / B6CA ratios. This can be indicative of degradation of BC during the transport from its source (either continental or marine). An alternative explanation may be that BC from surficial sediments in remote/deep sediments is older than in sites with high sedimentation rates. In

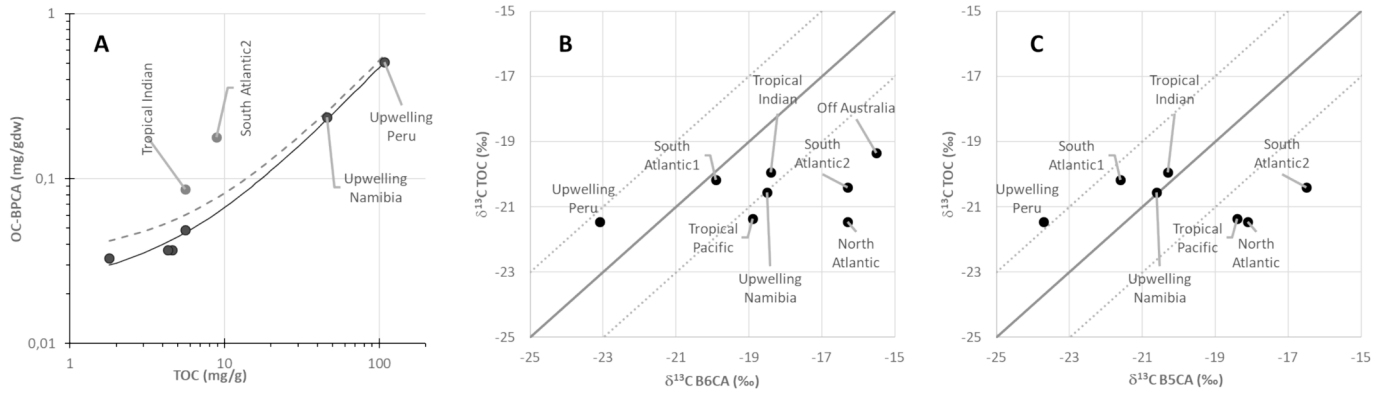

Fig. 7. Comparison of TOC and BC sedimentary composition. (A) The two linear regressions between the TOC and OC-BPCA were calculated with all samples (dashed line) and excluding grey samples (solid line). Comparison of $\delta^{13}C$ values with $\delta^{13}C$-B6CA (B) and δ13C-B5CA, respectively.

this case, the labile and more soluble component of the sedimentary BC may have had more time to oxidize and/or dissolve after reaching the ocean floor. Overall, the reduction of the B5CA / B6CA ratio with the distance from the BC source points to a progressive alteration of the BC composition during its transport and/or accumulation in deep sea sediments.

The $\delta^{13}C$ values measured for B6CA and B5CA ranged between −15.5 and –23.7‰. Isotopic values measured for B5CA (−16.5 — –23.7‰) were more negative than for B6CA (−15.5 — –23.5‰), with an averaged difference of 1.1‰. These small but significant differences may be indicative of different sources for the most refractory and highly polymeric fraction (B6CA, less negative values) and the less polymerized fraction (B5CA, more negative values). An alternative explanation is that the isotopic shift may be the result of diagenetic alteration that modified the isotopic composition of the more labile B5CA-producing fraction of the BC. In fact, studies based on the post-depositional oxidation of organic matter in turbidites proved that post-depositional diagenesis can shift the sedimentary $\delta^{13}C$-TOC signal by 0.3 — 2.5‰ toward more negative values (McArthur et al., 1992; Prahl et al., 2003). However, measured B6CA-to-B5CA isotopic differences do not covary with the sediment depth nor the B5CA / B6CA ratio. Accordingly, the causes for the approximately 1.1‰ difference between the isotopic composition of the B5CA and B6CA remain unexplained and should be further studied.

3.7. Marine and pyrogenic sources of BC_BPCA

The extremely strong correlation between TOC and BC_BPCA abundances in marine sediments from different oceanic regions and sedimentary environments points to a marine origin for the polycondensed aromatic fraction. Covariation of BC and TOC contents in soils, sediments, and DOM has been repeatedly reported in the literature, irrespectively of the methodology used to estimate BC (Reisser et al., 2016). This general pattern has been interpreted as indicating that commonly used BC methodologies (including BC_BPCA) are biased by the existence of a refractory fraction of non-pyrogenic organic matter in environmental samples (Zimmerman and Mitra, 2017). Accordingly, the association between BC content and PyrBC inputs is not straightforward and may lead to an large overestimation of the PyrC accumulated in soils, sediments and DOM (Zimmerman and Mitra, 2017; Coppola et al., 2022). In fact, some evidence has been reported on the existence of non-pyrogenic polycondensed aromatic materials in soil samples. Glaser and Knorr (2008), concluded that up to 25% of the BPCAs obtained in laboratory and field incubation experiments of soils were non-pyrogenic. Chang et al. (2018), observed that > 90% of BPCAs produced in some soil samples were associated with humic acids and concluded that they were not of pyrogenic origin. The conclusion is that quantitative studies that target the distribution of pyrogenic materials in the environments should address and correct for the potential interferences from the sedimentary matrix.

Oceanic sediments represent a good opportunity to differentiate diagenetic from pyrogenic BC_BPCA using their $\delta^{13}C$ signature. The $\delta^{13}C$ values of organic matter produced in the oceans (−19 to −23‰) are distinct from continentally derived organic matter produced by either C3 (−26 to −28‰) or C4 plants (−12 to −15‰). It should be noted that a combination of C3 and C4 sources may also produce an isotopic signal that can confounded with organic matter of marine origin. Therefore this possibility should be considered when interpreting $\delta^{13}C$ values in marine sediments. As detailed in Figs. 6 and 7, we found significant differences between the isotopic signatures of BC_BPCA and TOC. Measurements of $\delta^{13}C$_TOC varied over a short range (−19.3 — –21.5‰) and were generally consistent with the algal/marine origin of the sedimentary organic matter (Fischer, 1998). Measured $\delta^{13}C$_B6CA and $\delta^{13}C$_B5CA values showed a larger variability than $\delta^{13}C$_TOC (−15.5 — −23.7‰). Four sediment samples produced $\delta^{13}C$_BC_BPCA values outside the common range of oceanic particulate organic carbon (−15.5 — −18.5‰, Fig. 6 top, red circles). These samples were retrieved near the main global sources of atmospheric PyrC (Fig. 6, shadowed continental areas) indicating that the sedimentary BC originated from wildfires occurring in C4 dominated ecosystems. Large differences between the isotopic composition of TOC and BC_BPCA (up to 5‰) further supports the conclusion of a different origin for the TOC (mostly marine) and the condensed polymeric fraction (mostly C4_pyrogenic). Ecosystems dominated by C4 plants, such as the tropical savannas, are highly pyrogenic and responsible for the majority of pyrogenic materials emitted to the atmosphere (Randerson et al., 2005; Randersson et al., 2017; van der Werf et al., 2017). Accordingly, the isotopic composition of BC confirms the pyrogenic origin of the BC accumulated in four samples located under the direct inputs of air transported materials of pyrogenic origin.

High BC_BPCAs correlated with high TOC concentration values in sediments off Namibia and Peru indicate a dominance of marine sources to the BC in high productivity oceanic areas. In fact, TOC isotopic values measured for these sediments were consistent with a predominantly marine origin for the sedimentary organic carbon (Table 3), the $\delta^{13}C$_TOC value off Namibia being somewhat less negative than off Peru (−20.6 vs −21.5‰). In contrast, the BC isotopic signatures were markedly different in both samples (B6CA / B5CA $\delta^{13}C$ values: Namibia −18.5 / −20.6 vs Peru –23.1 / –23.7‰, respectively). In the case of the Peru upwelling sediment $\delta^{13}C$_BC was 1.6 — 2.2‰ more negative than $\delta^{13}C$_TOC, suggesting a predominantly marine contribution to the BC with a smaller contribution of combusted C3 plants. The existence of C3-derived pyrogenic material is consistent with the predominance of C3 plants in the western south American continent (Still et al., 2003). Since C4 ecosystems are not abundant in Peru and Chile, the isotopic signal measured in the adjacent marine settings cannot be explained by a

combination of C3 and C4 sources. Instead, the good correlation observed between the TOC and BC_BPCA sedimentary content confirms the marine origin of BC as indicated by δ^{13}C_BC measurements. The relative contribution of marine and C3-Pyr inputs can be estimated by assuming an isotopic mass balance. Assuming δ^{13}C values of −21‰ and −28‰ for the marine and Pyr-C3 endmembers, respectively, the contribution of the Pyr-C3 to B6CA / B5CA is approximately 30 / 39%. In contrast, the difference between δ^{13}C_BC and δ^{13}C_TOC off Namibia was in the opposite direction, δ^{13}C_BC being less negative than δ^{13}C_TOC, suggesting mixed marine and Pyr-C4 origin. In the Namibia sediment, the contribution of Pyr-C4 to the sedimentary B6CA / B5CA would be 28 / 4%, respectively (assuming −21 and −12‰ for the marine and Pyr-C4 endmembers, respectively). Again, the isotopic δ^{13}C_BC is consistent with the general dominance of C4-dominated ecosystems in the southwestern African continent.

4. Conclusions

We have adapted the different procedural steps of the BPCAs methodology to ensure the reproducible quantitative and isotopic (δ^{13}C) characterization of BC in marine sediments. This methodology has been applied to a set of 8 sediment samples representative of different oceanic areas. Remarkably, we found large concentrations of BPCAs in all sediments, including oceanic locations distant from continental areas. Both the covariation of BC and TOC content and their isotopic signature consistently indicate that a significant fraction of BC accumulated in marine sediments is of marine origin. Also, the relative proportion of the marine and pyrogenic contributions is highly variable among oceanic settings. The marine contribution can be largely dominant in sediments underlying high productivity areas and in remote sediments distant from the direct continental influence. However, BC can be mostly pyrogenic/continental in sites receiving large continental inputs such as the eastern tropical Atlantic. Therefore, calculation of PyC accumulation in marine sediments based on BC_BPCA may be unrealistic unless a correction for the marine contribution is included. This result is relevant for studies targeting the distribution of PyrC in the oceanic environment to avoid large inconsistencies in the global budgets (Coppola et al., 2022). In the case of marine systems, the relative proportion of diagenetic vs pyrogenic carbon can be evaluated by measuring δ^{13}C of BPCAs because of the marked isotopic differences between marine and continental sources.

CRediT authorship contribution statement

N. Penalva-Arias: Writing – original draft, Investigation, Formal analysis. **O. Teruel:** Validation, Formal analysis. **M. Raja:** Validation, Supervision. **A. Rosell-Melé:** Resources, Funding acquisition. **J. Villanueva:** Writing – review & editing, Writing – original draft, Supervision, Resources, Project administration, Methodology.

Declaration of competing interest

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

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.orggeochem.2024.104811.

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