

Article

Multiscale Variability of Atmospheric CO₂ at the Azores: Detecting Seasonal and Decadal Oscillations

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Abstract

Atmospheric carbon dioxide (CO₂) levels are rising globally, yet their multiscale variability in remote oceanic regions remains poorly characterized. This study examines a 45-year monthly CO₂ record (1980–2024) from the Azores, a subtropical North Atlantic site, using a spectral and statistical framework. The series was decomposed into high- and low-frequency components via Butterworth filtering and analyzed with the Correlogram-Based Periodogram (CBP) and Monte Carlo significance testing. The residual component robustly recovered the expected seasonal cycle (~12 months), validating the methodology. The trend component revealed an apparent enhancement in low-frequency spectral power, largely explained by the accelerating long-term increase. Control tests with a synthetic quadratic trend and polynomial detrending indicate a weak ~11-year enhancement in low-frequency power that is not robust under a red-noise (AR(1)) null. Segmented regressions showed a sustained and accelerating increase in CO₂ accumulation over the past four decades, consistent with Mauna Loa. These results demonstrate the importance of long-term monitoring in remote regions while highlighting both the potential and limitations of spectral methods for detecting weak low-frequency signals in greenhouse gas records.

Keywords: atmospheric CO₂; multiscale variability; seasonal cycle; decadal variability; spectral methods; greenhouse gases; Azores



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1. Introduction

The atmospheric concentration of carbon dioxide (CO₂) has increased dramatically since the onset of the industrial era, making it a key driver of global climate change. Long-term monitoring is essential to understand the dynamics of the carbon cycle and to detect shifts associated with both natural processes and anthropogenic activities. Despite extensive monitoring of atmospheric CO₂ at continental and coastal sites, its multiscale variability in remote oceanic regions remains poorly quantified and statistically underexplored. No previous study has rigorously assessed the decadal-scale variability of CO₂ in mid-ocean island environments such as the Azores using validated spectral methods, leaving an important gap in the understanding of how natural climatic oscillations interact with long-term anthropogenic trends.

Long-term baseline CO₂ observations at remote sites have been carried out for several decades under the National Oceanic and Atmospheric Administration's Climate Monitoring and Diagnostics Laboratory/Global Monitoring Laboratory global flask-sampling

network, which was specifically designed to target clean marine boundary-layer conditions and minimize local contamination. These global and hemispheric analyses (e.g., the National Oceanic and Atmospheric Administration's Climate Monitoring and Diagnostics Laboratory and the GLOBALVIEW-CO₂ project) have provided an essential reference for understanding atmospheric CO₂ trends and gradients across remote marine environments. Building on this established framework, the present study focuses on a regional mid-Atlantic site within this global network and aims to provide a statistically validated spectral characterization of multiscale variability rather than a reassessment of global trends already documented by NOAA-GML.

Global assessments such as the Global Carbon Budget have shown that while fossil emissions and oceanic uptake exhibit relatively smooth decadal trends, semi-decadal variability persists in the atmospheric CO₂ growth rate, reflecting coupled biospheric and climatic feedbacks [1].

Discrepancies between anthropogenic emission trends and atmospheric CO₂ growth rates have long indicated that short-term variability in oceanic and terrestrial sinks plays a crucial role in modulating observed concentrations [2].

Beyond its monotonic increase, CO₂ exhibits oscillatory behavior at multiple time scales, reflecting complex interactions between the atmosphere, biosphere, and ocean systems [3–6]. Long-term records have revealed seasonal patterns, hemispheric gradients, and interannual variability linked to ocean–atmosphere exchange, biospheric activity, and climate modes such as El Niño and the North Atlantic Oscillation (NAO) [7]. Recent satellite-based studies have confirmed that seasonal modulation is present even in remote subtropical oceanic regions, highlighting the role of local meteorological and biospheric feedbacks [8].

Seasonal variations in atmospheric CO₂ are well documented across continental and coastal regions [3,4,9,10], yet comparatively fewer studies have targeted island or mid-ocean environments. Ref. [11] showed that semi-enclosed coastal systems such as Jeju Island act as net CO₂ sources with pronounced spatial and seasonal variability, whereas Ref. [12] demonstrated that volcanic lakes on Pico Island (Azores) emit primarily biogenic CO₂ and CH₄, underscoring the importance of isolated oceanic settings for constraining the global carbon budget.

Recent studies from Mediterranean WMO/GAW stations such as Lamezia Terme have demonstrated that background CO₂ series exhibit significant positive trends and strong seasonality when adequately filtered to remove local influences [13]. Such findings reinforce the need for continuous, high-quality atmospheric records in island environments to capture regional-scale carbon variability.

While seasonal cycles of CO₂ are well characterized globally, far less attention has been paid to multiscale periodicities in remote island environments. Such locations provide unique opportunities to observe background atmospheric conditions with minimal continental influence, making them ideal for detecting low-frequency variability and long-range transport signals. However, interpreting these signals can be challenging due to the combined effects of oceanic transport, meteorological variability, and episodic pollution events.

While global datasets have long revealed the complex temporal behavior of atmospheric CO₂ [7,9] regional inverse analyses for the North Atlantic [14] demonstrate that climatic oscillations such as the NAO and AMV imprint decadal signatures on air–sea carbon exchanges.

Ref. [15] illustrate how abrupt changes in the interhemispheric CO₂ gradient, such as the 0.8 ppm step observed between 2009 and 2010, and large-scale transport anomalies in the equatorial upper troposphere can modulate the apparent carbon balance on decadal scales.

Recent oceanographic analyses have confirmed that the North Atlantic plays a dominant role in the global oceanic uptake of anthropogenic CO₂. Ref. [16] reported a 60% increase in the Atlantic anthropogenic carbon inventory between 1990 and 2020, largely driven by ventilation variability in the subpolar North Atlantic and Labrador Sea. These decadal fluctuations in oceanic carbon storage mirror the multi-scale variability observed in atmospheric CO₂ at mid-Atlantic sites such as the Azores, suggesting a coupled ocean–atmosphere control on regional carbon dynamics.

Overturning circulation accounts for most of the anthropogenic CO₂ storage in the North-East Atlantic, supporting the hypothesis that the low-frequency variability observed in the Azores record may reflect basin-scale ventilation processes [17].

In addition to oceanic processes, geochemical analyses of Azorean volcanic paleosols indicate that island weathering can represent episodic but efficient CO₂ sinks during interglacial stages [18] reinforcing the view of oceanic islands as active components in the regional carbon cycle.

Within this dynamic oceanic corridor, the Azores constitute a natural observatory for capturing such multiscale variability.

Despite growing interest in CO₂ time series, no previous study has rigorously quantified decadal-scale variability in Azores CO₂ records using statistically validated spectral methods. Here, we address this gap by analyzing a 45-year monthly CO₂ record from the Azores using a robust multiscale spectral framework. We apply empirical decomposition to separate high- and low-frequency components, followed by the Correlogram-Based Periodogram (CBP) and Monte Carlo significance testing, to characterize both the seasonal cycle (as a methodological benchmark) and the less-explored decadal-scale variability.

The originality of this study lies not in confirming the well-known increase or the strong seasonal cycle of atmospheric CO₂, but in applying a rigorous multiscale and statistically validated framework to a long-term record from a remote oceanic station. By combining the Correlogram-Based Periodogram (CBP) with Monte Carlo significance testing, synthetic quadratic controls, polynomial detrending, and band-pass filtering, we are able to distinguish genuine low-frequency variability from artefacts of the accelerating anthropogenic trend. This approach allows, for the first time at the Azores site, a quantification of the amplitude of the decadal signal (~0.26 ppm peak-to-peak), demonstrating its statistical detectability but also its limited climatic relevance. In doing so, the study provides a methodological contribution on how to robustly assess weak oscillatory features in strongly trending greenhouse gas time series.

In this sense, the novelty of this work is twofold: (i) providing the first statistically validated spectral assessment of decadal-scale CO₂ variability at a mid-Atlantic island background site using a CBP + Monte Carlo AR(1) framework; and (ii) quantifying the amplitude of the decadal band and discussing its physical plausibility in the context of North Atlantic circulation. This includes a mechanistic discussion linking the detected low-frequency variability to basin-scale processes associated with the North Atlantic Oscillation (NAO) and the ocean–atmosphere ventilation patterns that it modulates across the North Atlantic.

2. Materials and Methods

2.1. Study Area and Dataset

The study focuses on atmospheric CO₂ measurements collected at the Azores archipelago. This archipelago is in the North Atlantic Ocean, between latitudes 36.5° N and 39.5° N and longitudes 24.5° W and 31.5° W. It comprises nine volcanic islands, grouped into three geographic groups: the western group (Flores and Corvo), the central group (São Jorge, Terceira, Graciosa, Faial, and Pico), and the eastern group (São Miguel and

Santa Maria). The Azores occupy a strategic position in the context of Atlantic climatology, lying within a transitional zone between tropical and polar air masses. Due to their insular location in the subtropical North Atlantic basin, the islands are directly influenced by large-scale atmospheric systems such as the Azores High, polar fronts, extratropical depressions, and, occasionally, subtropical cyclones. This complex interaction between the islands' orography and atmospheric dynamics results in a temperate maritime climate, characterized by low annual thermal amplitude, high precipitation levels, elevated relative humidity, and prevailing winds throughout the year.

Given these characteristics, the Azores archipelago has been selected as a strategic location for long-term atmospheric monitoring within the NOAA Cooperative Global Air Sampling Network [19]. The atmospheric CO₂ record analyzed in this study originates from the AZR surface flask site, located on Terceira Island and operated under NOAA's Global Monitoring Laboratory (GML), which has coordinated flask-based trace gas sampling since the late 1960s. Long-term measurements at this site provide valuable insights into background marine air composition with minimal continental interference.

The AZR station is strategically located in the North Atlantic Ocean, within the Azores archipelago (between 36.5° N and 39.5° N, and 24.5° W to 31.5° W), allowing for the observation of marine boundary layer air masses with minimal local anthropogenic influence Figure 1.

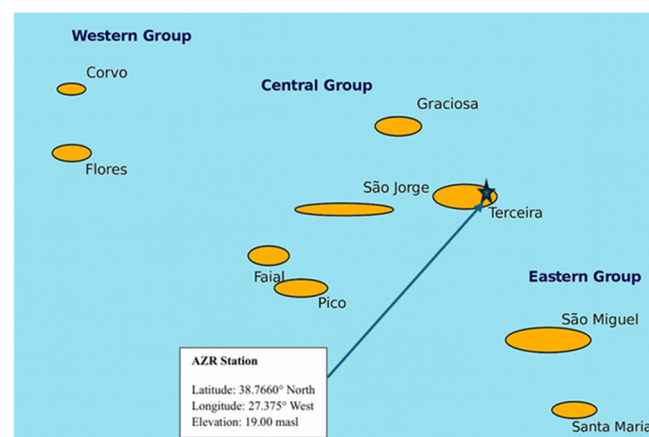


Figure 1. Location of the AZR surface flask sampling site in the Azores archipelago, North Atlantic Ocean. The station is located on Terceira Island (Central Group) at 38.7660° N, 27.3750° W, with an elevation of 19.0 m above sea level (masl). The archipelago comprises nine volcanic islands grouped into Western, Central and Eastern groups. The AZR station is part of NOAA's Cooperative Global Air Sampling Network and provides long-term observations of marine boundary layer carbon dioxide (CO₂) concentrations under minimal continental influence.

Air samples are collected weekly using a standardized flask sampling protocol, which involves filling paired glass flasks with ambient air and shipping them to the central NOAA laboratory in Boulder, Colorado, for high-precision analysis.

This methodology ensures data consistency and comparability across the global network. Measurements at the AZR site have been conducted since 1979, resulting in a multi-decadal record suitable for evaluating both seasonal cycles and low-frequency climatic oscillations in atmospheric CO₂. The dataset used in this study corresponds to monthly average concentrations, based on rigorous laboratory analysis and quality control procedures applied by NOAA GML. Air samples are collected approximately weekly from network sites, and monthly means are calculated using discrete flask measurements that have passed through strict laboratory calibration and quality control procedures.

The station provides long-term monitoring data that is considered representative of clean marine boundary layer conditions. Although referred to as “monthly averages,” the CO₂ concentration values are not continuous monthly means but represent the average of the available high-quality flask measurements that have passed through NOAA GML’s quality control and calibration procedures.

After collecting, the air samples from the AZR site are analyzed at the NOAA Global Monitoring Laboratory (GML) in Boulder, Colorado. The Measurement Laboratory uses high-precision instrumentation and standardized protocols to determine trace gas concentrations, including CO₂, with rigorous quality assurance and calibration procedures. This ensures that the measurements are consistent, reproducible, and traceable to international reference standards, making the AZR CO₂ record suitable for climate research and long-term variability assessments. According to NOAA GML documentation, CO₂ concentrations are measured using calibrated non-dispersive infrared (NDIR) analyzers. Measurement accuracy is approximately ± 0.2 ppm, and measurement precision is typically ± 0.1 ppm, based on repeated analysis of standard gases and flask pairs. These values are traceable to the World Meteorological Organization (WMO) CO₂ mole fraction scale. [20].

Prior to decomposition and spectral analysis, missing values in the CO₂ time series were addressed. A total of 29 data points, originally flagged as -999.99 , were linearly interpolated using the average of adjacent valid values, given the regular time spacing of the dataset. This approach preserves the continuity of the time series without introducing artificial trends.

This interpolation ensured continuity of the time series while preserving the statistical integrity of long-term trends and spectral characteristics.

The raw dataset comprises 3149 individual flask observations spanning 1980–2024, which were quality-controlled and subsequently aggregated into monthly means. Although the full period covers 540 months, flask sampling at the AZR site was not continuous in the early years, resulting in a total of 435 months with valid data, see Supplementary Figure S1 for monthly sampling coverage. Descriptive statistics in Table 1 are therefore based on these aggregated monthly mean values.

Table 1. Descriptive statistics of atmospheric CO₂ concentrations ($\phi(\text{CO}_2)$ /ppm) at the AZR surface flask site (Azores) and based on aggregated monthly mean values spanning 1980–2024. The dataset comprises 435 valid monthly means derived from quality-controlled weekly flask observations (N = 3149) provided by NOAA GML.

Statistic	$\phi(\text{CO}_2)$ /ppm
Mean	377.92
Minimum	333.55
25th Percentile (Q1)	354.64
Median (Q2)	374.58
75th Percentile (Q3)	401.67
Maximum	426.8
Range	93.25
Interquartile Range (IQR)	47.04
Skewness	0.22
Kurtosis	−1.21

To investigate the underlying temporal structure of the CO₂ record, the monthly time series was decomposed into low- and high-frequency components, allowing for the

identification of distinct modes of variability across different time scales, as described in the following section.

Sampling Protocol and Representativeness Filters

Paired flask samples at AZR are collected under NOAA/Carbon Cycle Greenhouse Gas Group standard operating procedures, with weekly sampling targeting marine boundary-layer background conditions. Site operators select sampling windows to minimize local influences, based on local meteorology and air-mass history, including wind speed/direction and the absence of obvious nearby sources; any potentially impacted samples are flagged in the NOAA–GML database and excluded by the Quality Assurance/Quality Control. Concentrations are determined at GML–Boulder under traceable WMO calibration scales with documented precision/accuracy. To increase transparency, Table S1 (Supplement) summarizes typical local sampling windows and preferred wind sectors used at AZR to target clean marine air during the study period, and the exact quality flags applied in our screening.

The documentation sources used to construct Table S1 are listed in Table S2 (Supplement), including NOAA–GML Standard Operating Procedures and the AZR site metadata.

2.2. Decomposition of the Time Series

To isolate different modes of variability in the atmospheric CO₂ time series, we performed an empirical decomposition into two components: a low-frequency trend and a high-frequency residual. This approach enables a more accurate characterization of seasonal and decadal periodicities.

The trend component was extracted using a zero-phase Butterworth low-pass filter with a cutoff frequency of 0.05 cycles/month, equivalent to a 20-month period. This threshold was chosen to attenuate seasonal and interannual fluctuations while preserving slower trends.

The filter was applied using the `filtfilt()` function from the `scipy.signal` Python (Version 3.11.8) module, which performs forward and reverse filtering to eliminate phase distortion while preserving the amplitude and timing of the signal.

The residual component of the time series is obtained by subtracting the low-frequency trend from the original CO₂ signal. This operation isolates short-term variability, including seasonal and interannual fluctuations, from the long-term evolution of atmospheric CO₂, Equation (1).

$$\text{Residual}(t) = \text{CO}_2\text{-original}(t) - \text{CO}_2\text{-trend}(t) \quad (1)$$

This type of smoothing is particularly suitable for climatic time series with nonstationary behavior and aligns with best practices for low-pass filtering under appropriate boundary constraints, as discussed by Mann [21]. The low-pass filtered output represents the trend component, capturing the slow-varying background signal, including long-term growth and decadal oscillations.

Filtering was performed using the `filtfilt()` function from the `scipy.signal` module in Python, which applies the operation in both forward and reverse directions. This zero-phase filtering prevents phase distortion and preserves the temporal structure and amplitude of the signal.

A normalized cutoff frequency of 0.05 cpm, equivalent to a period of approximately 20 months, was selected to suppress seasonal and interannual variability while retaining low-frequency trends.

To isolate the underlying temporal structures of the atmospheric CO₂ series, pseudo-EMD was performed using a zero-phase Butterworth low-pass filter. Although the Empirical Mode Decomposition (EMD) method was not applied directly, we refer to the filtering

process as a “pseudo-EMD” to indicate its functional similarity: the use of a zero-phase Butterworth low-pass filter allows us to separate the original CO₂ signal into a slow-varying trend and a high-frequency residual, akin to the empirical separation of intrinsic mode functions in EMD. This terminology reflects the conceptual goal of isolating temporal components without assuming stationarity or linearity. This approach effectively attenuates short-term fluctuations while preserving the long-term behavior of the signal, allowing us to extract a low-frequency trend component and a high-frequency residual. Similar statistical decomposition strategies have been applied to temperature time series in Europe to identify trends, harmonic structures, episodic fluctuations, and extreme events, thereby enabling a clearer separation between long-term and short-term variability [22].

Alternative methods, such as Singular Spectrum Analysis (SSA), have also proven effective for decomposing environmental time series into trend and oscillatory components, particularly in the presence of nonlinearity or nonstationarity [23]. Similar decomposition strategies based on spectral analysis and model selection (e.g., additive vs. multiplicative frameworks) have also been applied to CO₂ time series [24], demonstrating the value of descriptive approaches for capturing seasonal regularity.

After separating the CO₂ time series into trend and residual components, each was subjected to spectral analysis using the Correlogram-Based Periodogram (CBP) to identify dominant periodicities at different time scales.

2.3. Spectral Analysis: Correlogram-Based Periodogram

To detect dominant periodicities in the decomposed CO₂ time series, we employed the Correlogram-Based Periodogram (CBP) method, a robust spectral analysis technique well-suited for nonstationary and noisy environmental datasets. Unlike traditional periodograms that rely on direct Fourier transformation of the original signal, the CBP first computes the autocorrelation function of the time series and then applies a Fast Fourier Transform (FFT) to the resulting correlogram. Throughout this study, frequencies were initially computed in cpm to match the monthly resolution of the time series. However, for interpretability, dominant periodicities are reported in terms of their corresponding periods (in months), which better reflect the temporal resolution and avoid sub-month interpretations.

Formally, the CBP estimates spectral power $S(f)$ by applying a discrete Fourier transform to the autocorrelation function $R(\tau)$ of the time series (Equation (2)).

$$S(f) = \left| \sum_{\tau=0}^L R(\tau) e^{-2\pi i f \tau} \right| \quad (2)$$

where

- $R(\tau)$ is the Spearman rank correlation between the original time series X_t and its lagged version $X_{t+\tau}$;
- τ is the time lag;
- f is the frequency, expressed in cpm, corresponding to the inverse of the period in months (e.g., 0.083 cpm = 12-month cycle);
- $S(f)$ is the estimated spectral density at frequency f .

In this study, autocorrelation was estimated using Spearman’s rank correlation coefficient, a non-parametric method more robust to nonlinearities, trends, and outliers features commonly found in geophysical time series. The use of Spearman correlation enhances the robustness of the spectral estimate by relaxing assumptions of linearity and stationarity.

The Correlogram-Based Periodogram (CBP) yields a spectral power distribution in which peaks correspond to dominant periodicities embedded in the original signal. A prominent peak observed at 0.083 cpm (equivalent to a 12-month cycle) reflects the strong

annual modulation of atmospheric CO₂. Another peak near 0.0083 cpm (≈ 120 months) indicates the presence of a decadal-scale oscillation. These spectral features highlight the multiscale structure of the time series.

The CBP method has proven particularly effective in environmental and climate sciences due to its ability to extract meaningful periodicities from relatively short or nonstationary records. Its integration with Monte Carlo-based significance testing, as performed in this study, enhances the statistical robustness of periodicity detection and interpretation. This methodological framework follows best practices in climatic time series analysis, which recommend multiple complementary spectral approaches to distinguish signal from stochastic noise in nonstationary environmental datasets [25].

This approach aligns with established guidelines for climatic time series analysis, which emphasize the importance of spectral methods capable of handling nonstationarity, noise, and signal overlaps in complex environmental datasets [26].

However, the detection of spectral peaks alone is not sufficient; rigorous statistical validation is required to confirm their significance, as detailed in the following section.

2.4. Significance Testing

We evaluated spectral significance using a Monte Carlo test under a red-noise (AR(1)) null, following recommendations for climatic time series with strong autocorrelation [26,27]. Specifically, we fitted an AR(1) model to a quadratic-detrended version of the low-frequency (trend) component to ensure stationarity [5,28], and generated 1000 AR(1) surrogate series of equal length [27]. AR(1) parameters (ϕ, σ) were estimated by OLS using the regression of x_t on x_{t-1} after quadratic detrending of the trend component [5,28]. Random seeds were set for reproducibility. We adopt a one-sided test with significance level $\alpha = 0.05$, and report the observed band-power fraction φ_D , the surrogate mean $\pm$ sd, and the Monte Carlo p -value ($M = 1000$).

We used the band-power integrated over the decadal band (9–12 years; 108–144 months), computed as the sum of spectral power within $[1/144, 1/108]$ cpm, as a test statistic. We also report the band-power fraction (band-power divided by total spectral power) to normalize across runs [25,26]. The one-sided p -value was estimated as the proportion of surrogates whose band-power fraction was greater than or equal to the observed one [27,29]. This red-noise null avoids the liberal behavior of a white-noise null at low frequencies for autocorrelated climate series [26,27]. For completeness, we also computed the traditional global g -statistic; however, decadal-band inference is based on the band-power test under the AR (1) null [25–27].

Definitions used for the decadal band are shown in Equation (3):

$$B_D = \sum_{f \in D} S(f), \quad \varphi_D = \frac{B_D}{\sum_f S(f)}, \quad D = \{f : 1/144 \leq f \leq 1/108 \text{ cpm}\} \quad (3)$$

Here, $S(f)$ is the spectral power, as defined in Section 2.3.

The decadal-band test was applied to the low-frequency (trend) component, whereas the seasonal band (~ 12 months) was tested on the residual component using the same framework.

In Section 3, the global peak-ratio statistic g is defined as shown in Equation (4):

$$g = \frac{\max(S(f_i))}{\sum_{i=1}^N S(f_i)} \quad (4)$$

where $S(f_i)$ denotes the spectral power at frequency f_i and N is the number of Fourier frequencies.

We pre-specified the decadal band as 9–12 years and assessed robustness with 10–12 and 8–13-year bands.

3. Results

Having established the statistical significance of key spectral features using the CBP and Monte Carlo testing, we now present the main findings of the multiscale analysis. These include a strong seasonal cycle, a decadal enhancement oscillation, and a long-term upward trend in atmospheric CO₂ concentrations at the Azores site.

3.1. Characterizing the Temporal Variability of Atmospheric CO₂

A complete time series of atmospheric CO₂ concentrations measured at the AZR surface flask site between 1980 and 2024 is presented in Figure 2.

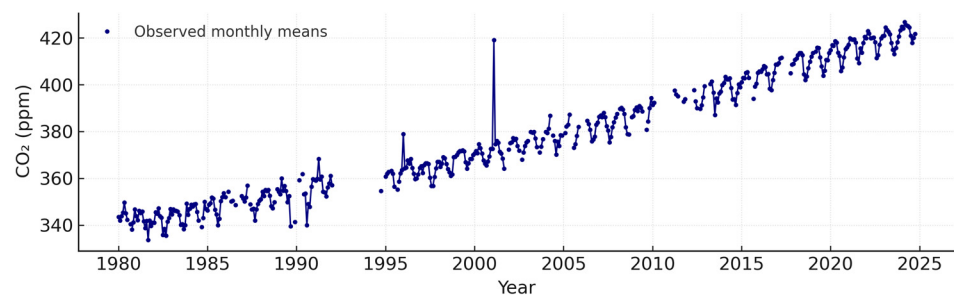


Figure 2. Monthly atmospheric CO₂ at AZR (1980–2024). Markers show observed monthly means that passed NOAA–GML Quality Assurance/Quality Control; line segments connect only consecutive months and leaving gaps where data are not available. Interpolated values used solely for spectral pre-processing are not displayed.

To avoid misinterpretation of collection gaps, Figure 2 shows only measured monthly means, connecting consecutive months and leaving visible gaps; filled values (e.g., −999.99) are excluded from display and used only for pre-processing steps where continuity is required.

Additional information on the temporal coverage of flask sampling events is provided in the Supplementary Materials (Figure S1), which displays the number of observations per year and month at the AZR site (1980–2024). This heatmap illustrates variations in data coverage and confirms the irregular sampling frequency typical of long-term baseline records.

This long-term record reveals both short-term seasonal fluctuations and a clear long-term increasing trend in CO₂ levels, consistent with global atmospheric patterns.

As seen in Figure 2, CO₂ concentrations exhibit a clear seasonal pattern (intra-annual variability) and a long-term increasing trend. Although interdecadal variability is not immediately visible in the raw series, it becomes apparent after decomposition and spectral analysis, as shown in Figures 6 and 7. This justifies the application of multiscale methods to isolate hidden low-frequency structures.

To further contextualize the long-term evolution of atmospheric CO₂, Figure 3 presents the decadal distribution of monthly concentrations at the AZR site. This boxplot representation captures changes in central tendency and dispersion across successive decades, illustrating the persistent upward shift in CO₂ levels observed over the 45-year monitoring period.

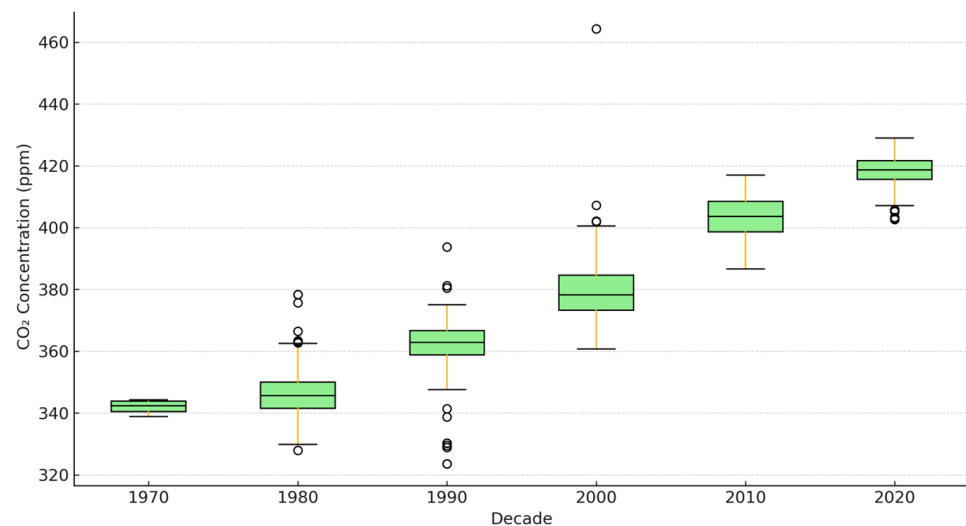


Figure 3. Decadal distribution of atmospheric CO₂ concentrations measured at the AZR surface flask site (Azores). Boxplots represent the interquartile range (IQR) for each decade, with the horizontal line indicating the median. Whiskers extend to the minimum and maximum values within $1.5 \times \text{IQR}$, while values beyond this range are shown as potential outliers. The plot illustrates a persistent rise in atmospheric CO₂ over successive decades, consistent with global trends driven primarily by anthropogenic emissions.

In addition to long-term decadal changes, interannual variability in atmospheric CO₂ is also evident. Figure 4 presents the annual distribution of CO₂ concentrations at the AZR site, providing a finer temporal resolution that captures year-to-year fluctuations. This plot highlights not only the sustained increase in median values over time, but also the presence of potential extremes, further supporting the need for spectral analysis to disentangle underlying cyclical patterns.

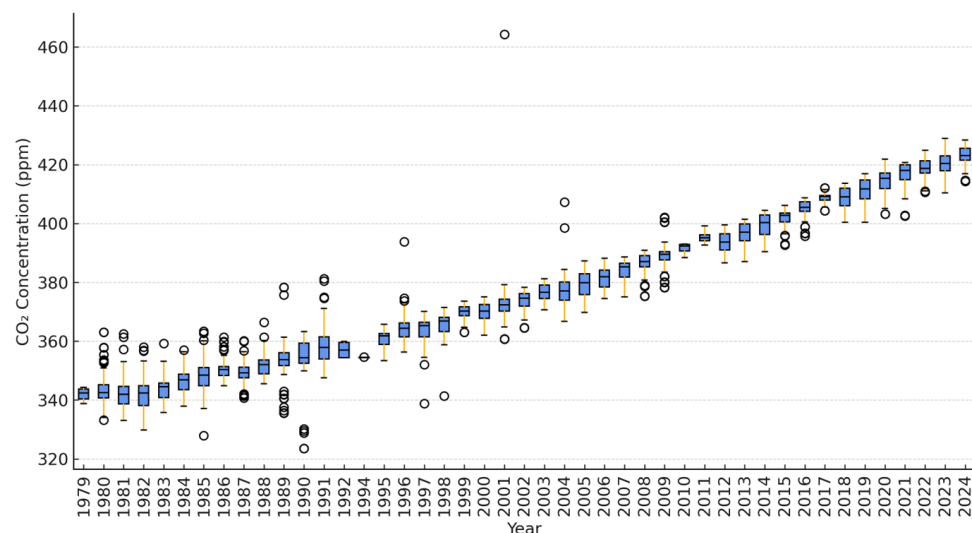


Figure 4. Annual distribution of atmospheric CO₂ concentrations measured at the AZR surface flask site (Azores). Each box represents the interquartile range (IQR) for a given year, with the horizontal line indicating the median CO₂ concentration. Whiskers extend to the minimum and maximum values within $1.5 \times \text{IQR}$, while individual points beyond this range are shown as potential outliers. The plot illustrates interannual variability superimposed on a persistent long-term upward trend.

To investigate the temporal structure of short-term fluctuations in atmospheric CO₂, we applied the Correlogram-Based Periodogram (CBP) to the high-frequency residual of the monthly series. The spectrum shows a prominent peak at ≈ 12 months (≈ 0.083 cpm),

consistent with the seasonal cycle, which is statistically significant under an AR(1) red-noise null (Monte Carlo $M = 1000$; $p < 0.001$). The magnitude and significance of this seasonal peak are shown in Figure 5 and discussed below.

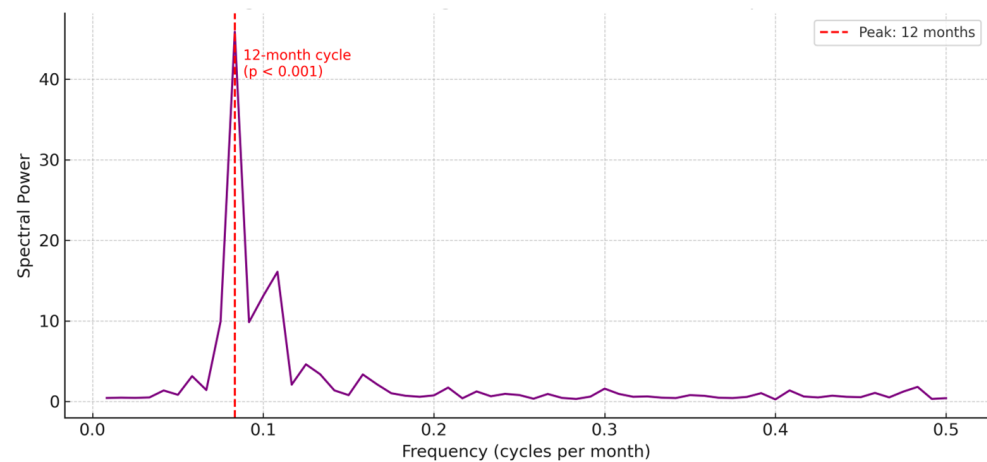


Figure 5. Correlogram-Based Periodogram (CBP) of the residual component of the monthly CO₂ time series at the AZR surface flask site (Azores), computed using a maximum lag of 120 months. The residual series was obtained by subtracting a low-frequency trend extracted via a Butterworth low-pass filter (cutoff = 0.05 cycles/month). A prominent spectral peak at ~ 0.083 cycles/month (12-month period) indicates a strong seasonal cycle and which is statistically significant under an AR(1) red-noise null (Monte Carlo $M = 1000$; $p < 0.001$).

The residual component analysis revealed a robust seasonal cycle with a periodicity of approximately 12 months (~ 0.083 cpm), consistent with the global seasonal variability of atmospheric CO₂. Although expected, this result is important for two reasons: (i) it validates the ability of the decomposition and Correlogram-Based Periodogram (CBP) to recover known periodicities, ensuring confidence in the detection of less evident signals such as the decadal oscillation; and (ii) it characterizes the amplitude and phase of seasonality at the Azores site, enabling comparisons with other oceanic observatories and the assessment of potential regional influences, such as the North Atlantic Oscillation (NAO) or sea surface temperature (SST) anomalies. Previous modeling and observational studies [30–32] have linked seasonal CO₂ variability to environmental drivers such as SST, vegetation dynamics, and climate oscillations (e.g., El Niño), reinforcing the role of biosphere–climate interactions in shaping short-term fluctuations. These processes, while beyond the main scope of this study, provide important context for interpreting the observed seasonal cycle at the Azores site.

Having confirmed the presence of a statistically significant annual cycle in the residual component, we now turn to the analysis of slower variability embedded in the long-term trend of the CO₂ series.

3.2. Spectral Analysis of Decadal Variability in CO₂

The CBP applied to the low-frequency trend component revealed an enhancement in spectral power centered between ~ 120 and 132 months (~ 0.0076 – 0.0083 cpm), consistent with decadal-scale variability (Figure 6). An enhancement in low-frequency power is present around ~ 11 years; however, under an AR(1) red-noise null, the decadal band-power fraction (9–12 yr) is not statistically significant (Monte Carlo $M = 1000$; $\phi_D = 0.088$; $p \approx 0.65$).

This longer-term fluctuation, embedded in the background evolution of atmospheric CO₂ concentrations, may be linked to decadal-scale climate variability or solar-related forcing. Previous studies have identified ~ 11 -year signals in climate records that are often

associated with the solar cycle [33], but given our significance framework we refrain from attribution.

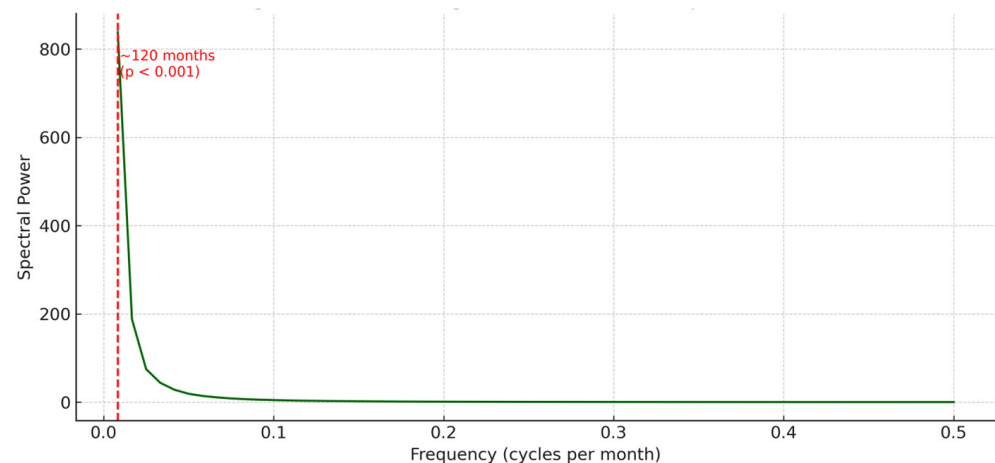


Figure 6. Correlogram-Based Periodogram (CBP) of the trend component. A low-frequency enhancement around ~10–11 years is visible; under an AR(1) red-noise null, the decadal band-power fraction (9–12 yr) is not statistically significant (Monte Carlo $M = 1000$).

An enhancement in low-frequency power is present around ~11 years; however, under an AR(1) red-noise null, the decadal band-power fraction (9–12 yr) is not statistically significant (Monte Carlo $M = 1000$; $\phi_D \approx 0.088$; $p \approx 0.65$). For completeness, the global peak-ratio statistic for the trend spectrum is $g \approx 0.118$ (Equation (4)). Control experiments with a synthetic quadratic trend confirmed that much of the low-frequency spectral power originates from the accelerating background increase. After polynomial detrending, a weak residual enhancement remained in the 9–12-year band (~0.26 ppm peak-to-peak), but it did not reach significance under the AR(1) band-power test and is therefore not robust. In addition to potential solar influences, this decadal-scale variability may reflect internal modes of ocean–atmosphere coupling, such as those observed in the Pacific basin [34], and may represent the impact of low-frequency climatic oscillations on the global carbon cycle. Furthermore, external forcings such as major volcanic eruptions have been shown to interact with background climate variability on decadal timescales, potentially altering atmospheric CO₂ dynamics through feedbacks in the ocean–biosphere system [35].

Comparing the CBP spectra of the residual and trend components (Figure 7) clearly shows the separation of dominant periodicities: a robust seasonal cycle (~12 months) in the residual, and a low-frequency enhancement around ~10–11 years in the trend; however, under an AR(1) red-noise null the decadal band-power fraction (9–12 yr) is not statistically significant (Monte Carlo $M = 1000$).

This reinforces the value of the decomposition approach for isolating overlapping temporal processes in atmospheric CO₂ records.

Although this oscillation does not drive the overall upward trend in atmospheric CO₂, it may superimpose temporary accelerations or slowdowns, complicating linear trend interpretations. Identifying such variability is therefore essential for separating natural low-frequency signals from the persistent anthropogenic increase and for improving the representation of carbon–climate feedbacks in models.

We now examine the long-term growth rate of atmospheric CO₂ at the AZR site.

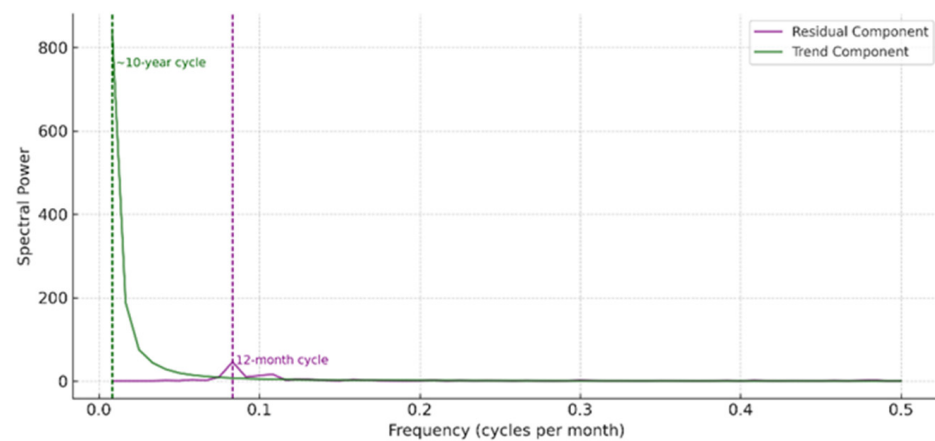


Figure 7. Correlogram-Based Periodogram (CBP) comparing the residual and trend components of the monthly CO₂ time series at the AZR surface flask site (Azores). The residual component captures the dominant seasonal cycle (~0.083 cpm). The trend component shows a low-frequency enhancement around ~10–11 years; under an AR(1) red-noise null, the decadal band-power fraction (9–12 yr) is not statistically significant (Monte Carlo M = 1000). Dashed vertical lines mark the seasonal (~12 months) and decadal (~10–11 years) bands.

3.3. Decadal CO₂ Growth Rate

Annual mean CO₂ concentrations from the AZR site (1980–2024) were analyzed using segmented linear regressions for each decade and the most recent sub-decade. Table 2 summarizes the results.

Table 2. Decadal and recent-period trends in atmospheric CO₂ concentrations at the AZR station (1980–2024).

Period	Growth Rate (ppm/year)	Standard Error	R ²	<i>p</i> -Value
1980–1989	1.33	±0.16	0.89	3.95×10^{-5}
1990–1999	1.57	±0.29	0.8	0.00105
2000–2009	1.99	±0.08	0.99	8.89×10^{-9}
2010–2019	2.24	±0.16	0.96	5.27×10^{-7}
2020–2024	2.16	±0.19	0.98	0.00138

Growth rates increased from 1.33 ± 0.16 ppm/year in the 1980s to 2.24 ± 0.16 ppm/year in the 2010s, with a slight decline to 2.16 ± 0.19 ppm/year during 2020–2024, within the margin of error. All regressions show high coefficients of determination ($R^2 \geq 0.8$) and statistically significant *p*-values.

For comparison, the same analysis was applied to the Mauna Loa record (Table 3). Growth rates rose from 1.57 ± 0.10 ppm/year in the 1980s to 2.54 ± 0.08 ppm/year in 2020–2024, with $R^2 \geq 0.95$ across all intervals.

The consistency between AZR and Mauna Loa trends confirms that the Azores record reflects global background CO₂ accumulation. Segmenting the analysis avoids the bias of fitting a single trend to an accelerating series and highlights the progressive intensification of CO₂ growth over the last four decades.

Table 3. Decadal and recent-period trends in atmospheric CO₂ concentrations at the Mauna Loa station (1980–2024).

Period	Growth Rate (ppm/year)	Standard Error	R ²	<i>p</i> -Value
1980–1989	1.6	±0.1	0.95	2.1×10^{-6}
1990–1999	1.5	±0.1	0.97	6.7×10^{-7}
2000–2009	1.9	±0.1	0.99	3.2×10^{-9}
2010–2019	2.4	±0.1	0.99	7.8×10^{-10}
2020–2024	2.5	±0.1	0.99	3.4×10^{-4}

4. Discussion

The spectral and statistical analyses presented in the previous sections revealed both seasonal and decadal-scale oscillations embedded in the atmospheric CO₂ record from the Azores. This study provides the first statistically validated spectral assessment of atmospheric CO₂ variability in a mid-Atlantic Island environment. Unlike previous descriptive or short-term analyses, the application of the Correlogram-Based Periodogram (CBP) combined with Monte Carlo testing enables a robust detection and quantification of both seasonal and low-frequency components in a strongly trending greenhouse gas record. This methodological framework highlights the originality of the present work, offering new empirical insight into the temporal structure of background CO₂ variability at a remote marine site.

In this section, we interpret these findings in light of the broader scientific literature, starting with a descriptive overview of the dataset. Each component of the time series is then examined in detail to elucidate the climatic, oceanographic, and biospheric mechanisms that may underlie the observed multiscale variability.

4.1. Interpretation of Statistical Features in the CO₂ Record

The AZR surface flask record provides a clear view of long-term atmospheric CO₂ evolution in a remote mid-Atlantic location. Rather than reiterating descriptive statistics, the interpretation focuses on the structural and temporal features that shape the series.

A statistically significant structural break was detected around 1995 using the Chow test ($F = 266.04$, $p < 1.1 \times 10^{-16}$). This coincides with NOAA's designation as the WMO Central Calibration Laboratory for CO₂, ensuring traceability to primary reference standards and improving global measurement consistency. The timing also aligns with a broader acceleration in global emission rates after 1990, suggesting that the breakpoint reflects both an instrumentation improvement and a real intensification of atmospheric CO₂ accumulation [36].

The overall range of 93.25 ppm across 45 years highlights the magnitude of enrichment in a clean marine boundary layer setting, while the relatively symmetric distribution supports the reliability of the dataset for trend and variability analyses. By identifying and accounting for this structural change, subsequent trend and spectral analyses can more accurately distinguish between natural variability and the persistent anthropogenic signal.

Building on these statistical features, the next section examines the decadal and annual distribution patterns of atmospheric CO₂ at the AZR site.

4.2. Visual Patterns in Decadal and Annual Distributions

The boxplots in Figures 3 and 4 represent the decadal and annual distributions of atmospheric CO₂ concentrations at the AZR surface flask site (Azores). Both clearly illustrate a consistent and progressive rise in atmospheric CO₂ over time. The decadal plot highlights

a systematic upward shift in both the median and the interquartile range (IQR) from the earliest decades to the most recent ones. This pattern reflects the accumulation of CO₂ in the atmosphere, aligning with global trends driven primarily by fossil fuel combustion and land-use changes.

The annual boxplots provide finer temporal resolution, revealing year-to-year variability superimposed on the long-term trend. While short-term fluctuations are evident, possibly influenced by ocean-atmosphere interactions, volcanic activity, or regional transport, the overall pattern remains one of gradual increase. Notably, the annual medians increase steadily, and the presence of occasional outliers becomes more frequent in recent years, suggesting enhanced variability or increased observational sensitivity. Together, these visualizations support the conclusion that atmospheric CO₂ levels at the mid-Atlantic AZR station are increasing in accordance with global observations. They further underscore the value of long-term, high-precision monitoring networks in detecting both broad trends and fine-scale variations in greenhouse gas concentrations.

The pronounced peak in $\phi(\text{CO}_2)$ around 2001 (Figures 2–4) is not currently attributed to a documented change in sampling or instrumentation at AZR according to GML metadata. We tentatively attribute it to large-scale circulation anomalies (e.g., a strong positive phase of the NAO) or transient transport events, consistent with the sensitivity of mid-Atlantic sites to synoptic forcing.

The identification of distinct periodicities in the CO₂ time series at the Azores site offers insight into the multiscale processes governing atmospheric carbon variability in an oceanic island context.

4.3. Seasonal Cycle in Atmospheric CO₂

The ~12-month cycle detected in the residual component Figure 5, is consistent with the well-established seasonal variability of atmospheric CO₂ [5]. Although the Azores experience a temperate maritime climate with relatively mild thermal seasonality, their position in the mid-latitudes (36–39° N) ensures distinct annual variations in radiation, photoperiod, and circulation patterns. These factors contribute to a measurable seasonal modulation of atmospheric CO₂, consistent with other Northern Hemisphere oceanic observatories.

While expected, its clear identification after decomposition confirms the ability of the CBP framework to recover known periodicities, thereby reinforcing confidence in the detection of subtler low-frequency signals such as the decadal oscillation. This seasonal pattern also provides a baseline for comparing the amplitude and phase of CO₂ variability at the Azores with other oceanic monitoring sites, and for assessing potential regional influences from environmental drivers such as sea surface temperature (SST) anomalies, vegetation dynamics, and large-scale climate oscillations (e.g., ENSO, NAO) [18–20].

By validating the methodology and ensuring the separation of high- and low-frequency variability, the seasonal signal serves as a reference point for interpreting the more complex decadal-scale variability examined in Section 4.4.

4.4. Decadal Signal in the Trend Component of Atmospheric CO₂

The spectral analysis of the low-frequency trend component revealed a low-frequency enhancement at ~10–11 years. Rather than a sharply defined peak, the signal appears as a broad feature, suggesting slowly varying background variability. Under an AR(1) red-noise null, the decadal band-power fraction (9–12 yr) is not statistically significant; therefore, we interpret it as a weak, non-robust modulation of negligible amplitude (~0.26 ppm peak-to-peak), rather than a persistent periodicity. This behavior is illustrated in Figure 6.

Additional control analyses were performed to evaluate the robustness of this signal. A synthetic quadratic trend, mimicking the long-term acceleration of CO₂ but without

oscillations, reproduced much of the low-frequency enhancement, indicating that the raw spectrum partly reflects the background growth. After polynomial detrending, however, a weak residual enhancement remained in the 9–12-year band, but it did not reach significance under the AR(1) red-noise band-power test, with an amplitude of only ~0.26 ppm peak-to-peak. These calculations were carried out following standard procedures but are not shown in detail here.

The identification of this low-frequency oscillation raises the possibility that large-scale climate modes, such as the Atlantic Multidecadal Oscillation (AMO) and the North Atlantic Oscillation (NAO), modulate atmospheric CO₂ variability at the Azores site. Both have been shown to influence ocean–atmosphere CO₂ exchange by altering wind patterns, surface temperatures, and upper-ocean circulation in the North Atlantic [37,38]. The signal may thus reflect climate-induced variations in the rate at which the ocean absorbs or releases CO₂ on multiyear timescales.

Previous modeling and observational studies demonstrated that decadal modulations in North Atlantic CO₂ uptake are strongly influenced by the North Atlantic Oscillation (NAO), with positive phases reducing air–sea CO₂ flux in the eastern basin [37]. During positive NAO phases, enhanced westerlies and warmer subtropical inflows decrease solubility and ventilation in the eastern North Atlantic, weakening the regional CO₂ sink, whereas negative NAO phases promote colder surface waters and enhanced carbon uptake. Recent CMIP6 simulations confirm that decadal variability in North Atlantic CO₂ fluxes is largely driven by subpolar ventilation and overturning circulation [39], while tracer-based analyses reveal that long-term storage of anthropogenic CO₂ in North Atlantic water masses follows similar decadal adjustments linked to circulation variability [40]. Comparable decadal-scale fluctuations have also been identified in surface-ocean carbon records from the subtropical Atlantic, such as at the Bermuda BATS station, where a weak ~11-year cycle reflects coherent basin-scale coupling between atmospheric forcing and oceanic uptake [41].

In addition to surface exchange processes, longer-term changes in the storage of anthropogenic CO₂ in North Atlantic water masses may also contribute to the observed decadal variability [40]. Oceanic warming, in particular, reduces CO₂ solubility and can disrupt air–sea gas exchange, further amplifying long-term fluctuations in atmospheric CO₂ concentrations [42].

Although these decadal oscillations do not drive the overall upward trend in CO₂, they can modulate the pace of accumulation, creating temporary accelerations or slowdowns that complicate linear trend interpretation. Identifying such oscillatory behavior is therefore essential for understanding natural variability superimposed on anthropogenic forcing and for improving long-term projections of the carbon cycle.

The coexistence of seasonal and decadal cycles revealed in the trend and residual components calls for a comparative assessment. We address this in the following section through a joint interpretation of their CBP spectra.

4.5. Comparison of Seasonal and Decadal Cycles in the CBP Spectrum

The CBP spectra of the residual and trend components (Figure 7) reveal distinct dominant periodicities: a ~12-month seasonal cycle in the residual component and a broad low-frequency enhancement (~10–11 years) in the trend component. The seasonal signal likely reflects biospheric activity and hemispheric-scale atmospheric transport patterns, consistent with long-range temporal correlations and scaling behavior reported in CO₂ records [43]. The decadal variability is compatible with large-scale climate modes, such as the Atlantic Multidecadal Oscillation (AMO) and North Atlantic Oscillation (NAO), which

can modulate ocean–atmosphere CO₂ fluxes through changes in wind regimes, sea surface temperature, and upper-ocean circulation [38,44–47].

The coexistence of these two periodicities highlights the multiscale nature of atmospheric CO₂ variability at the AZR site. Seasonal and decadal oscillations arise from distinct physical mechanisms and operate on different time scales, but together they shape the temporal structure of background CO₂. Recognizing and separating these signals is essential for improving model representations of the carbon cycle and for distinguishing natural variability from the persistent anthropogenic trend. This multiscale perspective provides the basis for examining decadal trends in CO₂ accumulation, as discussed in Section 4.6.

4.6. Decadal Trends in CO₂ Accumulation

Average annual growth rates for successive decadal and sub-decadal periods were calculated from annual mean CO₂ concentrations at the AZR site using segmented linear regression. The results, summarized in Tables 2 and 3, reveal a statistically significant acceleration in CO₂ accumulation over the last four decades.

At the AZR site, the growth rate increased from 1.33 ppm/year in the 1980s to 2.24 ppm/year in the 2010s, with a slight decrease to 2.16 ppm/year in the 2020–2024 period. This small decline remains within the margin of error and does not indicate a reversal of the long-term trend. Similar behavior was observed in the Mauna Loa series, where the growth rate rose from 1.57 ppm/year in the 1980s to 2.54 ppm/year in the most recent period. These findings confirm the persistent and accelerating nature of atmospheric CO₂ accumulation at both regional and global scales.

Segmented regression by period offers a more accurate depiction of the long-term trend compared to fitting a single linear model across the entire time series. This approach avoids bias caused by recent acceleration and allows for the identification of inflection points or regime shifts. The agreement between the AZR and Mauna Loa records further supports the representativeness of the Azores as a reliable location for monitoring background atmospheric CO₂ levels.

These decadal trends emphasize the importance of sustained long-term observations and highlight the anthropogenic nature of the observed increase, providing a robust basis for improving future carbon cycle projections.

4.7. Methodological Considerations

The combined use of pseudo-EMD and the Correlogram-Based Periodogram (CBP) provided a robust framework for isolating and quantifying both short- and long-term variability in nonstationary climate time series. Unlike traditional Fourier-based spectral analyses, CBP is well suited to short records and benefits from the use of non-parametric autocorrelation estimators such as Spearman's rank.

Despite these advantages, CBP does not capture transient or evolving spectral features. In forecasting contexts, ARIMA-type models have been widely used for temperature and precipitation, but they rely on assumptions of stationarity and are not designed to detect hidden or multiscale periodicities, nor to assess the statistical significance of spectral peaks [48]. Alternative methods, such as wavelet transforms, are particularly effective in identifying multiscale and time-localized oscillations in nonstationary climate records [49]. Similarly, the discrete cosine transform (DCT) has been applied in spatial climate diagnostics to reduce spectral distortions from aperiodic boundaries [50].

Furthermore, recent work conducted in the Azores has demonstrated that large-scale atmospheric circulation patterns, particularly the North Atlantic Oscillation (NAO), significantly modulate surface pollutant concentrations (O₃, NO₂, and SO₂) at island scales [51]. These findings reinforce the regional sensitivity of atmospheric composition to

synoptic-scale climate variability, providing an observational complement to the multiscale CO₂ variability analyzed in this study.

In parallel, global modeling experiments indicate that under increased CO₂ forcing the NAO tends to become more positive and less variable, with a strengthened Azores High and enhanced subsidence over the North Atlantic [52] offering a broader dynamical context for the anomaly observed at mid-Atlantic sites such as the Azores.

The robustness of the present results was tested by re-running the decomposition and CBP analyses without interpolated values. The absence of significant differences in the location or magnitude of dominant peaks indicates that interpolation did not bias the detection of periodicities. Nonetheless, future studies could apply imputation methods optimized for autocorrelated climate time series to further validate this step.

The methodological framework applied here effectively identified dominant periodicities but would benefit from complementary time–frequency methods in future work, enabling the detection of non-stationary features whose amplitude or periodicity changes over time.

Based on these methodological considerations and the results obtained, the main conclusions of this study are presented in the following section.

5. Conclusions

This study applied a multiscale spectral approach, combining pseudo-EMD, Correlogram-Based Periodogram (CBP) analysis, and Monte Carlo significance testing, to characterize atmospheric CO₂ variability at the Azores site. By separating the monthly series into high- and low-frequency components, we identified distinct periodicities and quantified their contributions to long-term variability. The residual component showed a robust seasonal cycle (~12 months) consistent with biospheric fluxes and ocean–atmosphere exchanges while the trend component displayed a low-frequency (~10–11 years) enhancement largely explained by the accelerating long-term increase. Control tests (synthetic trend experiments, polynomial detrending, and band-power assessment) indicated that any decadal-band feature in the trend is weak and not robust under a red-noise (AR(1)) null, with a very small amplitude (~0.26 ppm peak-to-peak). Segmented trend analysis demonstrated a sustained and accelerating increase in CO₂ accumulation over the past four decades at both the AZR site and Mauna Loa.

These findings demonstrate that atmospheric CO₂ variability in remote oceanic regions is shaped by both short-term biological processes and long-term climatic modulations, underscoring the need to account for natural variability when interpreting trends and projecting future carbon dynamics.

Beyond its methodological contribution, this study provides empirical evidence that atmospheric CO₂ variability in remote oceanic regions results from the interplay between short-term biological and physical processes and longer-term climatic modulations. This finding emphasizes that natural variability remains an active component of the carbon-cycle signal even in background marine environments such as the Azores. Accounting for this multiscale variability is therefore essential when interpreting atmospheric CO₂ trends, assessing carbon-climate feedbacks, and improving projections of future greenhouse-gas dynamics under changing climate conditions.

The results highlight the value of long-term, high-quality measurements from remote stations such as the Azores for supporting global climate assessments, validating transport models, and informing climate policy. Future work should extend this framework to other observatories and greenhouse gases, integrating satellite observations (e.g., OCO-2, TROPOMI) and reanalysis data to better resolve spatial patterns and improve carbon-cycle modeling.

In addition to its scientific relevance, the results also have practical implications. The identification of multiscale CO₂ variability at a mid-Atlantic marine station supports the optimization of long-term greenhouse gas monitoring strategies and provides an empirical basis for improving atmospheric transport and carbon-cycle models. These findings can also assist in the calibration and validation of satellite missions (e.g., OCO-2, TROPOMI) and contribute to regional and global climate assessments by refining the representation of natural variability in policy-relevant carbon budgets.

Like any time-series study, this work has certain limitations. The analysis is constrained by the temporal resolution and length of the available record and focuses exclusively on atmospheric CO₂ without including other greenhouse gases or meteorological covariates. Future research should extend this multiscale framework to multi-gas datasets, integrate meteorological and oceanic parameters, and apply time–frequency methods such as wavelet analysis to capture evolving spectral behavior over time.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/atmos16111308/s1>, Figure S1. Heatmap showing the number of CO₂ flask observations per year and month at the AZR (Terceira Island, Azores) site for the 1980–2024 period. Each cell represents the total number of valid flask pairs collected in a given month, based on NOAA–GML QA/QC-filtered data. The color scale indicates the sampling density (from 0 to 20 observations per month), illustrating variations in data coverage through time and season; Table S1. Sampling metadata and representativeness filters applied to AZR flask CO₂ data (1980–2024); Table S2. References supporting the sampling protocol and metadata information used to construct Table S1. References [53–57] are cited in the supplementary materials.

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Abbreviations

The following abbreviations are used in this manuscript:

CO ₂	Carbon dioxide
AZR	Azores (NOAA Global Monitoring Laboratory flask site)
NOAA	National Oceanic and Atmospheric Administration
GML	Global Monitoring Laboratory
WMO	World Meteorological Organization
CBP	Correlogram-Based Periodogram
EMD	Empirical Mode Decomposition

NDIR	Non-Dispersive Infrared (analyzer)
NAO	North Atlantic Oscillation
SSA	Singular Spectrum Analysis
FFT	Fast Fourier Transform
AR (1)	Autoregressive Model of Order 1
SST	Sea Surface Temperature
IQR	Interquartile Range
ENSO	El Niño–Southern Oscillation
AMO	Atlantic Multidecadal Oscillation
ARIMA	Autoregressive Integrated Moving Average
DCT	Discrete Cosine Transform
OCO-2	Orbiting Carbon Observatory-2.
TROPOMI	Tropospheric Monitoring Instrument

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