

## Article

# Combined O<sub>3</sub> and NO<sub>2</sub> Pollution Reveals Widespread Nonlinear Impacts on Net Primary Productivity Across China's Terrestrial Ecosystems

Zhaosheng Wang  and Mei Huang \* 

Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, Beijing 100101, China; wangzs@igsrr.ac.cn

\* Correspondence: huangm@igsrr.ac.cn

## Abstract

Quantifying the large-scale impact of combined ozone (O<sub>3</sub>) and nitrogen dioxide (NO<sub>2</sub>) pollution on terrestrial carbon sinks remains a major challenge. Here, we develop a parsimonious yet robust empirical framework that leverages high-resolution remote sensing datasets (CHAP O<sub>3</sub>/NO<sub>2</sub> and MODIS NPP, 2008–2021) to characterize nonlinear threshold responses of terrestrial net primary productivity (NPP) across China's diverse ecosystems. Our observational analysis identifies only associative temporal relationships between annual NPP variability and pollutant concentrations, with NPP positively correlated with O<sub>3</sub> (Pearson's  $r = 0.714$ ,  $p < 0.01$ ) and negatively correlated with NO<sub>2</sub> ( $r = -0.599$ ,  $p < 0.05$ ). Notably, the ecosystem-specific threshold values (O<sub>3</sub>: 28,324–34,391  $\mu\text{g m}^{-3} \text{ yr}^{-1}$ ; NO<sub>2</sub>: 3646–4968  $\mu\text{g m}^{-3} \text{ yr}^{-1}$ ) are statistically derived from spatially aggregated pixel-level records across the full 14-year period, independent of the national annual time-series correlation analyses. Distinct from previous single-pollutant national evaluations, our study advances a novel analytical framework focusing on the interactive and combined impacts of O<sub>3</sub> and NO<sub>2</sub> co-exposure. The results demonstrate that NPP displays an increasing trend under low-level pollutant exposure but declines substantially once pollutant loads exceed the identified threshold ranges. Based on K-means clustering and segmented regression analyses, we estimate a national average NPP reduction of 17.4% per year ( $-0.68 \text{ Pg C yr}^{-1}$ ), resulting in a cumulative carbon loss of  $-9.48 \text{ Pg C}$  over the 14-year study period—equivalent to 2.45 years of China's total terrestrial carbon uptake. Among all ecosystem types, forestlands experience the largest cumulative carbon loss ( $-4.22 \text{ Pg C}$ ), with prominent loss hotspots concentrated on the Tibetan Plateau and Northwest China. This refined national-scale assessment of dual-pollutant impacts provides observation-based evidence of substantial terrestrial carbon sink degradation, underscoring the necessity of combined air pollution mitigation strategies to sustain ecosystem stability and climate mitigation targets.



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## 1. Introduction

Intensifying global warming and human activities are escalating atmospheric pollutant levels, altering their distribution, concentration, and toxicity, with profound impacts on ecosystems, particularly the terrestrial carbon cycle. Tropospheric ozone (O<sub>3</sub>) pollution significantly suppresses carbon uptake in terrestrial ecosystems (e.g., [1–9]), eroding their sink potential.

Early model projections indicate O<sub>3</sub> concentrations could rise 20–25% by 2050 [10] and 40–60% by 2100 [11,12] from current ~60 ppb levels. Notably, 60 ppb is already a high background level, and many regions in China (e.g., the North China Plain) have experienced concentrations persistently above this value, with accelerating upward trends [13,14]. An increase of one-quarter to 75 ppb would approach the upper limit of vegetation tolerance, posing an urgent threat to ecosystem health and productivity. Current O<sub>3</sub> pollution has already reduced global vegetation gross primary productivity (GPP) by 8–12%—equivalent to over twice China’s total vegetation GPP [15,16]—while China’s ecosystems alone exhibit 10–18% NPP reductions [17].  $NPP = GPP - R$ , where R is autotrophic respiration. Ignoring these effects risks underestimating China’s CO<sub>2</sub> absorption by a comparable margin, underscoring O<sub>3</sub>’s integral role in the carbon cycle and the need for mechanistic insights and improved assessment methods [18–23]. Nitrogen dioxide (NO<sub>2</sub>), a key nitrogen deposition component and O<sub>3</sub> precursor, further complicates this dynamic. Elevated nitrogen deposition influences carbon–nitrogen cycling (e.g., [24–27]), yet joint NO<sub>2</sub>–O<sub>3</sub> effects on plant growth and carbon regulation remain unclear. Plants absorb NO<sub>2</sub> via stomata, with ambiguous impacts on carbon assimilation [28], while NO<sub>2</sub> enhances O<sub>3</sub> formation, exacerbating pollution–vegetation interactions (e.g., [29–31]).

Combined O<sub>3</sub>–NO<sub>2</sub> exposures yield complex, often combined outcomes on carbon cycling. Joint exposure inhibits photosynthesis more severely than individual pollutants, inducing nonlinear declines in carbon uptake. This interaction modulates atmospheric oxidative capacity, with O<sub>3</sub> driving oxidative stress and NO<sub>2</sub> acting dually as a nutrient and stressor [30].

Despite remote sensing advances, robust methods for quantifying large-scale vegetation carbon losses from O<sub>3</sub>–NO<sub>2</sub> exposure are lacking. Field experiments confirm inhibitory effects, but upscaling is challenging; elucidating concentration thresholds impairing plant function is crucial for refined assessments.

China confronts acute challenges from rising O<sub>3</sub> and nitrogen deposition [27,32], which threaten ecological security and compromise the accuracy of national carbon sink estimates. While mechanistic models and chamber experiments have been invaluable, a critical gap persists in directly observing and quantifying the combined impacts of O<sub>3</sub> and NO<sub>2</sub> co-exposure on ecosystem carbon uptake at the national scale. This study addresses this gap by developing and applying a transparent, evidence-based framework designed specifically for large-scale evidence detection. We posit that a parsimonious approach, leveraging high-resolution remote sensing and robust statistical analysis, is not only adequate but necessary for this first-order, continental-scale assessment. Our primary objective is to identify and characterize spatially explicit, observation-based threshold patterns in NPP responses to combined O<sub>3</sub> and NO<sub>2</sub> exposure, and to develop a scalable empirical framework for large-scale ecosystem monitoring. This observational framework enables robust detection of associative nonlinear NPP responses across heterogeneous landscapes, while we explicitly acknowledge that our correlational design cannot fully isolate causal pollutant effects like controlled or quasi-experimental approaches. The thresholds and loss estimates presented here should therefore be interpreted as empirically grounded associations that require further validation through process-based modeling and manipulative studies.

## 2. Materials and Methods

### 2.1. Data Sources and Processing

To evaluate the combined impact of O<sub>3</sub> and NO<sub>2</sub> pollution on net primary productivity (NPP) across China’s terrestrial ecosystems, we integrated multi-source, long-term remote sensing and model-based datasets for the period 2008–2021.

High-resolution, daily surface O<sub>3</sub> and NO<sub>2</sub> concentration data were obtained from the ChinaHighAirPollutants (CHAP) archive (<https://weijing-rs.github.io/product.html>, accessed on 10 August 2026). We used the ChinaHighO3 dataset (CHAP\_O3\_D1K\_XXXX\_V2, 2008–2021) and the ChinaHighNO2 datasets (CHAP\_NO2\_D10K\_XXXX\_V1 for 2008–2018 and CHAP\_NO2\_D1K\_XXXX\_V2 for 2019–2021). These datasets were generated using artificial intelligence methods that fuse ground-based observations, satellite remote sensing, atmospheric reanalysis, and model simulations, providing reliable, nationwide pollution estimates. The CHAP data offer exceptional spatial and temporal coverage, essential for capturing the fine-scale variability of pollutants across China.

To quantify cumulative annual exposure, daily concentrations were aggregated into yearly cumulative metrics (units:  $\mu\text{g m}^{-3} \text{ yr}^{-1}$ ) using Climate Data Operators (CDO) software (version 2.3.0). The NO<sub>2</sub> data from 2008 to 2018 were originally at a 10 km resolution, while those from 2019 to 2021 were at 1 km.

Annual NPP data for 2008–2021 were derived from the Moderate Resolution Imaging Spectroradiometer (MODIS) product (MOD17A3HGF, available at <https://modis.gsfc.nasa.gov/data/dataproduct/mod17.php>, accessed on 10 August 2026). Land use and land cover (LULC) data for 2008–2020 were retrieved from the Google Earth Engine (GEE) platform. Both datasets have a spatial resolution of 1 km. Due to the unavailability of the LULC data for 2021, the 2020 dataset was used as a substitute—a standard practice in ecological modeling to maintain time-series continuity.

To examine the differential responses of major ecosystem types, the LULC categories were reclassified as follows: forest (types 1–5), shrub (types 6–7), grass (type 10), and crop (types 12 and 14). This classification enabled a stratified assessment of pollution impacts.

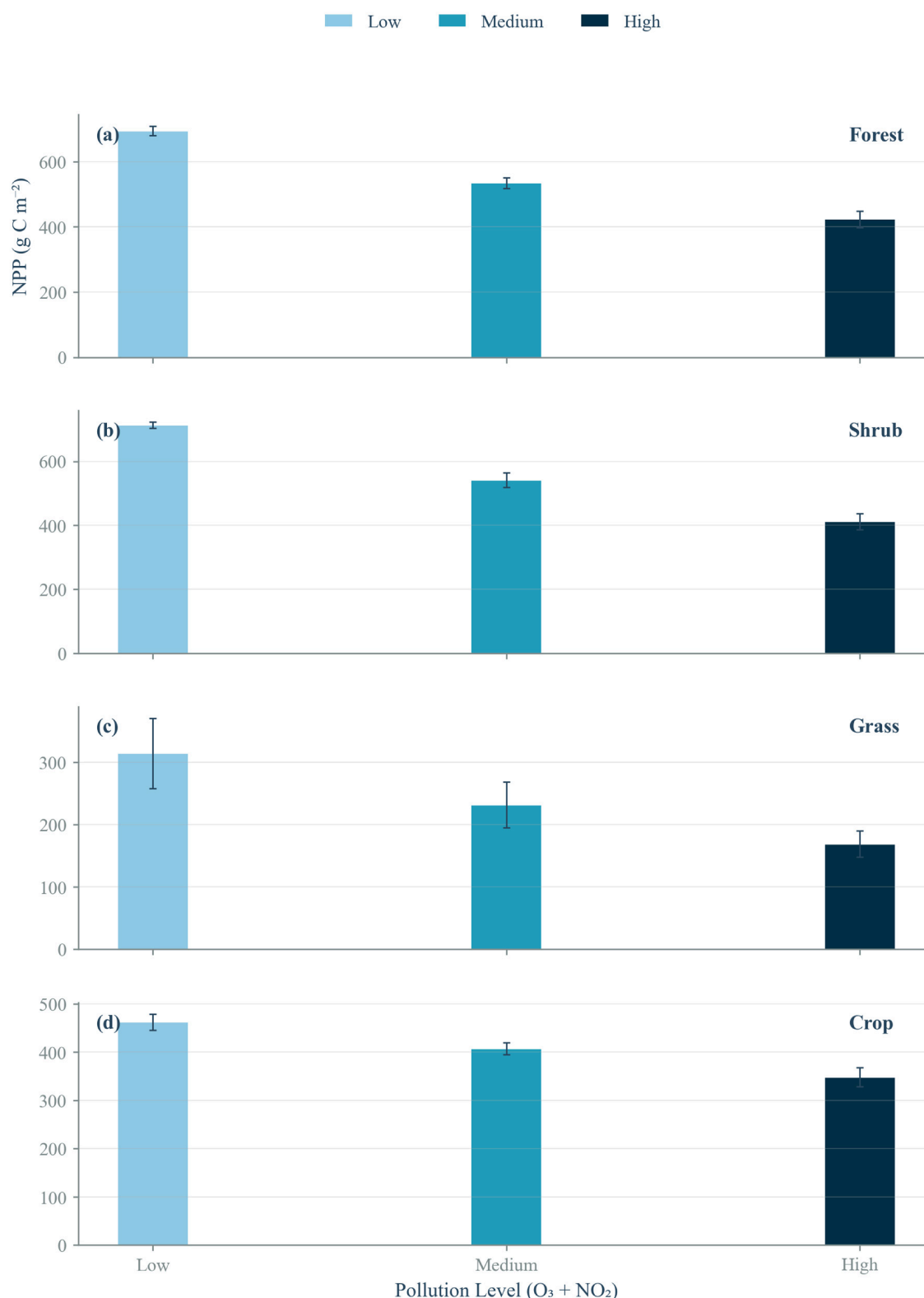
## 2.2. Analytical Framework for Large-Scale Evidence Detection

The methodological framework was designed with a primary objective: to detect and quantify the coherent signal of NPP loss in response to O<sub>3</sub> and NO<sub>2</sub> co-exposure from the substantial spatial and temporal heterogeneity of China's ecosystems. Rather than applying a complex, parameter-heavy model, we implemented a hypothesis-driven, data-centric approach that prioritizes interpretability and scalability. This framework strategically integrates two complementary analytical techniques: (1) K-means clustering to objectively stratify the continuous gradient of pollution exposure into ecologically interpretable regimes, and (2) segmented regression to quantitatively pinpoint the critical thresholds where the pollutant-NPP relationship undergoes a fundamental shift. The strength of this combined approach lies in its ability to extract clear, actionable insights directly from observational data, making it uniquely suited for generating first-of-its-kind, national-scale evidence.

### 2.2.1. Exposure Stratification via K-Means Clustering

To systematically classify NPP responses across varying atmospheric pollution conditions, we employed the K-means clustering algorithm, an unsupervised machine learning technique well suited for partitioning high-dimensional environmental data. The algorithm was applied to categorize the annual cumulative O<sub>3</sub> and NO<sub>2</sub> exposure levels across China (2008–2021) into three distinct regimes: low, medium, and high. Importantly, the classifications for O<sub>3</sub> and NO<sub>2</sub> were derived through separate one-dimensional K-means clustering rather than joint two-dimensional clustering. Since the one-dimensional clustering was performed separately for each pollutant based on their respective data distributions, variable standardization was unnecessary and would not have altered the independent classification results. Consequently, the order-of-magnitude difference between the two pollutants ( $\sim 10^4$  vs.  $\sim 10^3 \mu\text{g} \cdot \text{m}^{-3} \cdot \text{yr}^{-1}$ ) does not affect the clustering outcome. After the separate clustering

was completed, the combined “low/medium/high” pollution levels presented in Figure 1 were constructed by cross-tabulating the independently derived classifications.



**Figure 1.** Comparison of net primary productivity (NPP) across different pollution levels ( $\text{O}_3 + \text{NO}_2$ ) for four terrestrial ecosystems. (a) Forest, (b) shrub, (c) grass, (d) crop. The low–medium–high combined pollution clusters are derived from K-means clustering on joint  $\text{O}_3$ – $\text{NO}_2$  space; these levels do not imply synchronously high or synchronously low concentrations for both pollutants. See Table S1 for  $\text{O}_3$  and  $\text{NO}_2$  value ranges within each cluster.



K-means was selected for its computational efficiency, scalability, and effectiveness in partitioning data based on Euclidean distance—properties that align well with the gradient-like spatial distribution of air pollutants. The number of clusters ( $k = 3$ ) was predetermined to reflect ecologically meaningful exposure zones, consistent with established environmental risk classification frameworks. Cluster initialization was validated by minimizing the within-cluster sum of squares (WCSS) across 100 random initializations to ensure stability. The resulting NPP distributions within each cluster were then analyzed to identify inflection points in the pollutant-response relationship (see Section 2.2.2).

### 2.2.2. Segmented Regression for Threshold Quantification

To quantitatively identify the critical thresholds of  $O_3$  and  $NO_2$  exposure beyond which NPP begins to decline, we applied segmented (or piecewise) linear regression. This analysis was performed separately on two NPP subgroups for each vegetation type: pixels falling within the 95th–100th percentile bin (high-productivity vegetation) and the 48th–52nd percentile bin (medium-productivity vegetation). All threshold breakpoints were identified from bin-wise response curves generated from the 14-year (2008–2021) composite pixel-year average dataset; full sets of these hump-shaped bin curves stratified by forest, shrub, grass, and crop under both productivity subgroups are provided in Figures 2 and 3 and Supplementary Figures S2–S7, illustrating unimodal hump-shaped NPP–pollutant relationships across all ecosystems.

The segmented regression model was fitted on binned data constructed as follows: all pixel-year observations (2008–2021) were pooled, sorted by pollutant exposure concentration, and divided into 100 equal-width bins. For each bin, the median NPP was calculated to represent the typical vegetation response under the corresponding exposure level, yielding space-time aggregated bin-averaged response curves built on the 14-year composite record, as visualized in Figures 2 and 3 and Supplementary Figures S2–S7. The model can be formulated as:

$$NPP = \beta_0 + \beta_1 \times \text{Exposure}, \text{ for Exposure} \leq \text{Threshold}$$

$$NPP = \alpha_0 + \alpha_1 \times \text{Exposure}, \text{ for Exposure} > \text{Threshold}$$

where the parameters ( $\beta_0$ ,  $\beta_1$ ,  $\alpha_0$ ,  $\alpha_1$ ) and the breakpoint (Threshold) are estimated iteratively to minimize the overall residual sum of squares. The statistical significance of the segmented model and the slope difference between segments were assessed to test for the presence of a threshold response.

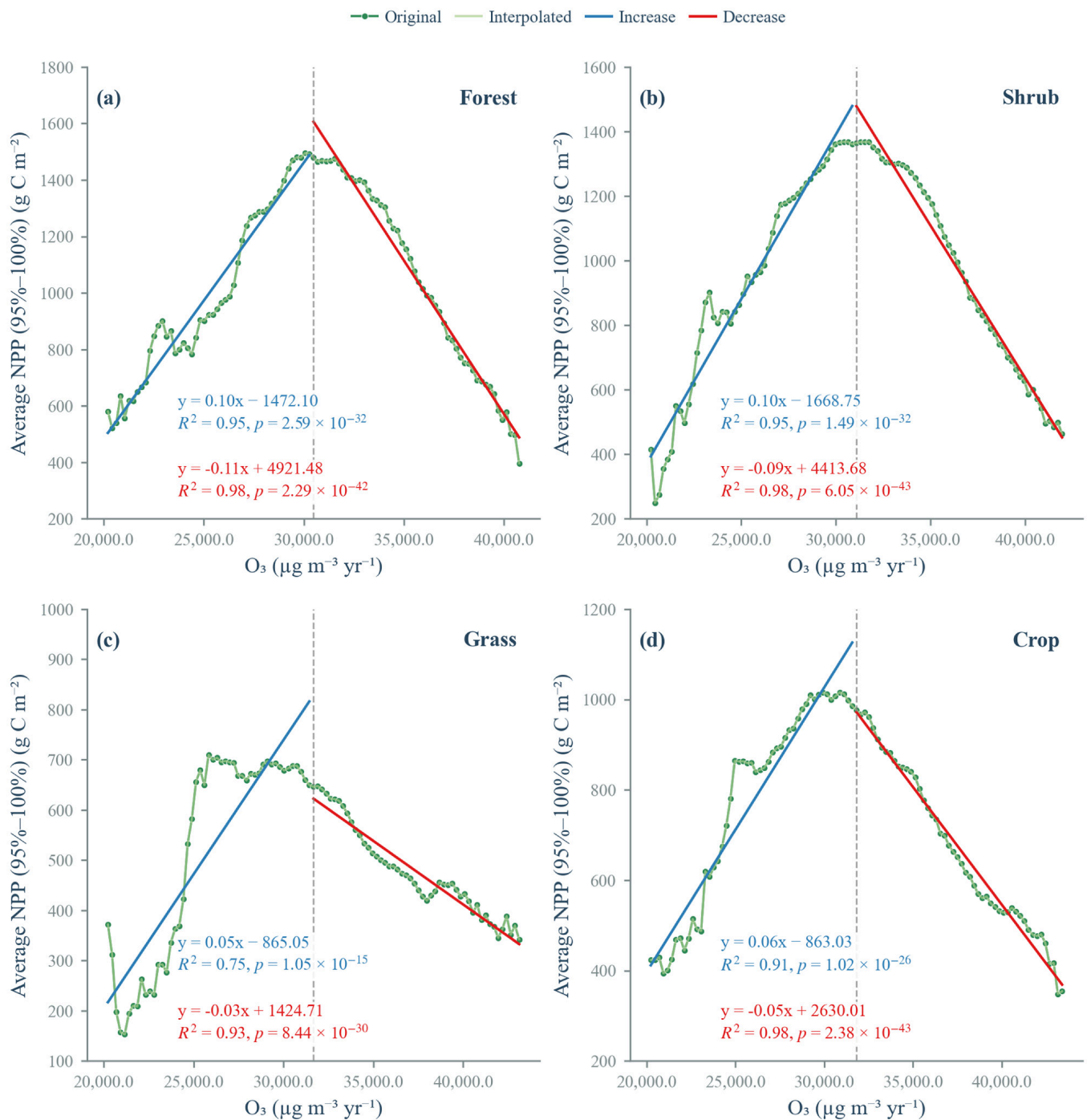
### 2.2.3. NPP Loss Model Development

Based on the identified thresholds, we developed a set of empirical models to estimate the NPP loss attributable to  $O_3$  and  $NO_2$  exposure for different ecosystem types. The models were constructed separately for the “Large NPP” and “Small NPP” ecosystem categories, as derived from the scatter plot distributions.

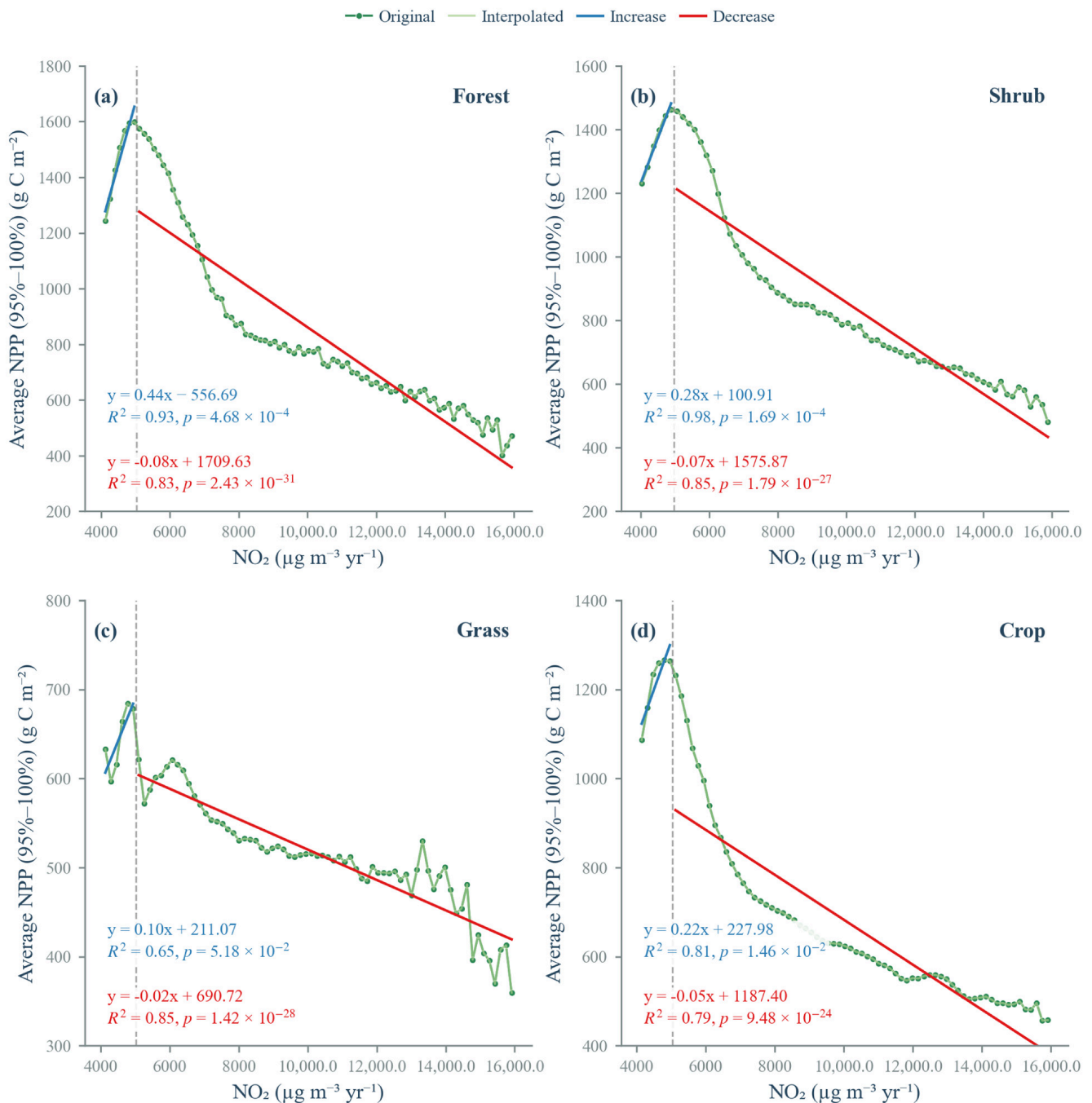
The general form of the model for NPP loss influenced by a single pollutant is

$$NPP\_loss = (NPP\_observed - NPP\_threshold) / NPP\_threshold \times 100\%$$

where  $NPP\_observed$  is the MODIS-derived NPP, and  $NPP\_threshold$  is the expected NPP at the critical threshold concentration, calculated from the segmented regression model.



**Figure 2.** The NPP variation curves for forest (a), shrub (b), grass (c), and crop (d) ecosystems within the 95–100% range of each O<sub>3</sub> pollution exposure bin. There are a total of 100 O<sub>3</sub> exposure bins. In the figure, the solid lines represent the segmented fitted lines, with green segments indicating the phase with no NPP loss and red segments indicating the phase with NPP loss. The intersection of the two lines represents the threshold point between NPP loss and no loss. The curves in the figure show the 14-year average results from 2008 to 2021. Binning was conducted year-by-year per ecosystem type; bin-level NPP values were averaged across 14-years to obtain composite response curves, on which segmented regression and threshold extraction were performed. Grey dashed lines denote threshold positions.



**Figure 3.** The NPP variation curves for forest (a), shrub (b), grass (c), and crop (d) ecosystems within the 95–100% range of each NO<sub>2</sub> pollution exposure bin. There are a total of 100 NO<sub>2</sub> exposure bins. In the figure, the solid lines represent the segmented fitted lines, with green segments indicating the phase with no NPP loss and red segments indicating the phase with NPP loss. The intersection of the two lines represents the threshold point between NPP loss and no loss. The curves in the figure show the 14-year average results from 2008 to 2021. Binning was conducted year-by-year per ecosystem type; bin-level NPP values were averaged across 14-years to obtain composite response curves, on which segmented regression and threshold extraction were performed. Grey dashed lines denote threshold positions.

For the combined effects of O<sub>3</sub> and NO<sub>2</sub>, an integrated model was developed to estimate the total NPP loss, accounting for the simultaneous exposure to both pollutants. In Equations (3) and (6), the combined loss is computed as the observed NPP relative to the average of two independently fitted counterfactual predictions (one from the O<sub>3</sub>-only

regression and one from the NO<sub>2</sub>-only regression). This averaging represents a symmetric compromise: in the absence of a well-constrained bivariate joint-response surface for concurrent O<sub>3</sub> and NO<sub>2</sub> stress, both single-pollutant counterfactual estimates are weighted equally, and no arbitrary priority is assigned to either prediction. This approach serves as a practical empirical approximation and does not formally capture interactive or true joint effects between O<sub>3</sub> and NO<sub>2</sub>. Divergence between the two sets of counterfactual predictions can emerge at the individual-pixel level and brings additional uncertainty into combined-pollutant loss quantification. The specific Equations (1)–(6) are presented in Section 3.2.3. To further integrate threshold detection with loss attribution and address climatic confounders, see the supplementary procedure in Section 2.2.4.

#### 2.2.4. Supplementary Procedure for Threshold Detection and Loss Attribution

Building upon the clustering (Section 2.2.1) and regression (Section 2.2.2) analyses, we systematically detail the analytical framework for nonlinear detection and attribution, applied across forest, grass, shrub, and crop ecosystems in China during 2008–2021.

For each year and ecosystem type, annual NPP ( $\text{g C m}^{-2} \text{ yr}^{-1}$ ), cumulative O<sub>3</sub>, and cumulative NO<sub>2</sub> ( $\mu\text{g m}^{-3} \text{ yr}^{-1}$ ) were extracted from all spatial grid cells across China from the CHAP and MODIS datasets.

NPP was plotted against cumulative O<sub>3</sub> and NO<sub>2</sub> separately to visualize their nonlinear functional relationships. Sorting was implemented over the full pooled pixel-year dataset; each observation corresponds to one grid cell in a single year. Supplementary Figures S2–S7 display complete bin-wise NPP response curves stratified by four vegetation types and two NPP subgroups (95–100% and 48–52% NPP percentiles). All curves exhibit consistent hump-shaped trajectories: NPP rises gradually to a peak before a sustained decline with increasing O<sub>3</sub>/NO<sub>2</sub> exposure. Inflection points (thresholds), marking the transition from rising to falling NPP, were detected using the segmented-regression workflow described in Section 2.2.2.

However, it is important to clarify that these curves were constructed by binning pixels according to pollutant concentrations within each year for each individual ecosystem type, extracting the corresponding NPP values for each bin, and then averaging the results across the 14 years (2008–2021) for each ecosystem type. In other words, each point on the curves represents the 14-year average response at a given pollutant concentration level, rather than a simple pooling of all pixel-year observations. This temporal averaging substantially smooths out interannual climate variability and ensures that the observed pattern reflects a climatological mean response rather than being driven by specific years with anomalous climate conditions.

Crucially, year-by-year bin-wise response curves (Supplementary Figures S4–S7) show that this rise-then-fall hump geometry persists across most individual years. This consistency reduces the concern that the aggregate hump shape arises merely from episodic, year-specific climatic anomalies. Nevertheless, this interannual consistency cannot rule out persistent spatial climatic confounding: if high-pollution pixels intrinsically occupy locations with lower climate-driven NPP potential, such spatial-gradient artifacts could reproduce the hump pattern in every single year. Therefore, the hump-shaped association remains observational and cannot be interpreted as definitive causal proof of pollutant-driven NPP loss. While spatial climatic confounding represents a plausible alternative explanation for the hump-shaped pattern, it is not the only possible interpretation of the observed concentration-response association.

Within the ascending segment of the response curve (from low NPP toward peak NPP), NPP variability is assumed to be primarily driven by baseline climatic drivers (temperature and precipitation). Post-threshold NPP reduction is interpreted as potential pollutant-

induced loss. This attribution represents a heuristic interpretative scheme and working hypothesis, rather than a strictly proven causal statement. It rests on the tentative premise that spatial climatic heterogeneity within a given vegetation type may be comparatively limited relative to the spatial gradient of pollutant exposure. Nevertheless, the hump-shaped patterns observed in the 14-year composite bin curves (Supplementary Figures S2–S7) could theoretically emerge purely from spatially structured climate gradients independent of pollutant stress, because high-O<sub>3</sub> grid cells do not geographically overlap with zones of maximum climatic NPP potential across China.

To quantify intra-ecosystem spatial climatic variation, we calculated spatial-domain coefficients of variation (CV; spatial variability, distinct from interannual temporal CV) for temperature and precipitation across pixels within each vegetation class (Supplementary Table S4). These statistics, computed from our pixel-level sampling, reveal substantial spatial climatic divergence within each ecosystem type across China; for example, grass shows a spatial CV of 165.44% for mean temperature. This confirms that climatic conditions cannot be regarded as spatially uniform within a single vegetation class. Consequently, climatic spatial confounding cannot be fully eliminated by stratifying only by vegetation type, and this structural limitation is elaborated in Section 4.4. The relative-loss calculation introduced in Section 2.2.3 was adopted for quantitative NPP-loss assessment.

Our analytical workflow adopts a tentative working assumption that climatic conditions are broadly comparable within each vegetation type across China, which aims to isolate pollutant effects and mitigate climatic confounding (partial correlation analyses in the Results further assist in disentangling these co-varying drivers). We explicitly emphasize that this is an approximate, non-universal assumption, not an inviolable foundational premise. As evidenced by Supplementary Table S4 and the broad spatial sampling captured in the 14-year composite bin curves of Supplementary Figures S2–S7, considerable within-type spatial variance in temperature and precipitation persists across China's broad geographic domains spanning subtropical, temperate, alpine, and arid zones. Unaccounted biophysical factors, including solar radiation, soil moisture, and anthropogenic land-management practices, may additionally introduce confounding effects for attribution, and these uncertainties are addressed in the discussion of study limitations. We did not explicitly simulate potential low-dose NO<sub>2</sub> fertilization effects, because published empirical response curves indicate net inhibitory effects dominate once exposure exceeds critical thresholds (Ashmore, 2005; Sheng and Zhu, 2019 [2,28]). Multiple sensitivity tests, including stratified data subsetting and  $\pm 10\%$  threshold perturbation, demonstrate stable model outputs, with relative loss deviations below 8% (Supplementary Table S2). A critical caveat reinforced by the 14-year composite bin curves and spatial-climate CV statistics: NPP loss magnitudes may be moderately overestimated when spatially divergent climatic signals covary with pollution gradients within the same ecosystem class, as the observed hump-shaped response curves cannot fully rule out alternative explanations originating from pure spatial climate gradients.

### 3. Results

#### 3.1. Changes in NPP Under Long-Term Joint Exposure to O<sub>3</sub> and NO<sub>2</sub> Pollutants

To detect the large-scale imprint of long-term O<sub>3</sub> and NO<sub>2</sub> pollution on ecosystem productivity, we analyzed annual variations in NPP, O<sub>3</sub>, and NO<sub>2</sub> from 2008 to 2021 for China's regional averages (Figure S1). Figure S1a shows a clear upward trend in NPP ( $R^2 = 0.83$ ), increasing by 10.3% from 413.2 g C m<sup>-2</sup> in 2008 to 455.9 g C m<sup>-2</sup> in 2021. Concurrently, Figure S1b illustrates a significant rise in annual O<sub>3</sub> exposure, reaching 36,219.4  $\mu\text{g m}^{-3} \text{ yr}^{-1}$  in 2021—1.2 times higher than in 2008, with an accelerated increase after 2017 ( $R^2 = 0.7$ ). Conversely, Figure S1c reveals a significant decline in NO<sub>2</sub> expo-



sure ( $R^2 = 0.48$ ,  $p = 0.006$ ), with a 13.2% reduction from an average of  $7398.9 \mu\text{g m}^{-3} \text{ yr}^{-1}$  (2008–2016) to  $6421.3 \mu\text{g m}^{-3} \text{ yr}^{-1}$  (2017–2021). NPP variation is significantly correlated with  $\text{O}_3$  (Pearson's  $r = 0.714$ ,  $p < 0.01$ ;  $n = 14$ ,  $\alpha = 0.05$ ) and inversely with  $\text{NO}_2$  (Pearson's  $r = -0.599$ ,  $p < 0.05$ ;  $n = 14$ ,  $\alpha = 0.05$ ), indicating that NPP changes are linked to  $\text{O}_3$  and  $\text{NO}_2$  exposure levels. Notably, these are raw Pearson correlation results calculated based on 14 sequential annual mean time-series data. No detrending processing or temporal autocorrelation-adjusted degrees of freedom correction was performed for the above raw correlation analyses, and further controlled partial correlation analyses eliminating confounding factors are presented in Section 4.1.

To further explore the combined effects of  $\text{O}_3$  and  $\text{NO}_2$  on net primary productivity (NPP), we employed K-means clustering to evaluate NPP variations across different ecosystems under low, medium, and high pollution exposure levels during the period 2008–2021 (Figure 1). Specifically, we systematically investigated the NPP response characteristics of four terrestrial ecosystems—forest, shrub, grass, and crop—under these three gradient levels of combined  $\text{O}_3 + \text{NO}_2$  pollution, with a primary focus on uncovering the divergent patterns of NPP loss among distinct ecosystem types.

Figure 1 illustrates that ecosystems differ in their sensitivity to combined  $\text{O}_3 + \text{NO}_2$  pollution, which is reflected by the heterogeneous trends of NPP along the pollution gradient. Notably, under high pollution exposure, NPP showed a decreasing trend in most ecosystems, suggesting the combined inhibitory effects of  $\text{O}_3$  and  $\text{NO}_2$  on vegetation productivity.

Results from two-way analysis of variance (two-way ANOVA) revealed that ecosystem type ( $F = 380.80$ ,  $df = 3, 156$ ,  $p < 0.001$ ), pollution exposure level ( $F = 246.07$ ,  $df = 2, 156$ ,  $p < 0.001$ ), and their interaction ( $F = 12.26$ ,  $df = 6, 156$ ,  $p < 0.001$ ) all exerted extremely significant effects on NPP. Moreover, effect size analysis using Cohen's  $f$  confirmed that all three factors induced large effects ( $f = 19.514$ ,  $15.687$ , and  $3.501$ , respectively), indicating that the impacts of combined pollution exposure on NPP are not only statistically robust but also ecologically meaningful.

Tukey's honestly significant difference (HSD) post hoc test further clarifies that all four ecosystem types suffer significant NPP loss with elevated  $\text{O}_3 + \text{NO}_2$  combined pollution exposure, yet marked discrepancies exist in the magnitude and threshold of loss. Under low pollution exposure, NPP in shrub ( $713.20 \text{ g C m}^{-2}$ ) and forest ( $694.10 \text{ g C m}^{-2}$ ) is significantly higher than that in crop ( $462.15 \text{ g C m}^{-2}$ ) and grass ( $314.54 \text{ g C m}^{-2}$ ), with no significant difference between shrub and forest ( $p = 0.9962$ ), and NPP loss in all ecosystems is relatively slight at this stage. Under medium pollution exposure, significant NPP loss occurs across all ecosystems, among which grass shows the most pronounced reduction (with a decrease of 26.3%), whereas shrub and forest still maintain relatively high productivity ( $541.57$  and  $534.21 \text{ g C m}^{-2}$ , respectively) with milder losses. Under high pollution exposure, NPP loss intensifies further; grass records the lowest NPP ( $168.93 \text{ g C m}^{-2}$ ) with a cumulative loss of 46.3%, while forest ( $423.05 \text{ g C m}^{-2}$ ) and shrub ( $411.70 \text{ g C m}^{-2}$ ) also exhibit substantial losses but retain comparatively high productivity.

Analysis of the interaction effect uncovers divergent tolerance thresholds to combined pollution exposure across ecosystems: crop and forest display significant NPP loss starting at the medium pollution level ( $p < 0.001$ ), significant loss in shrub only occurs at the high pollution level ( $p < 0.001$ ), and grass is more pollution-sensitive, showing significant loss already at medium exposure ( $p = 0.0201$ ). Collectively, the resistance of the four ecosystem types to  $\text{O}_3 + \text{NO}_2$  combined pollution ranks as follows: shrub > forest > crop > grass. Driven by their inherent functional and structural traits, different ecosystems face heterogeneous risks of NPP loss under combined  $\text{O}_3$  and  $\text{NO}_2$  pollution exposure.



### 3.2. Identify the Effect of Long-Term O<sub>3</sub> and NO<sub>2</sub> Joint Exposures on NPP

#### 3.2.1. Evidence of NPP Loss from Remote Sensing

Remote sensing provides direct evidence of NPP loss induced by combined O<sub>3</sub> and NO<sub>2</sub> exposure. Scatter plots for forest, shrub, grass, and crop ecosystems clearly illustrate the relationship between NPP and exposure from 2008 to 2021. The histogram analysis revealed that, across different ecosystems, the average NPP in the 95–100% and 48–52% bins first increased and then decreased as O<sub>3</sub> and NO<sub>2</sub> exposure levels rose. Outliers in scatter plots (e.g., in Figure S2c) were identified using Z-scores ( $>3$  or  $<-3$ ) and retained if attributable to real variability (e.g., regional extremes), but their influence was tested by refitting regressions without them, confirming minimal impact on overall trends.

#### Remote Sensing Evidence of NPP Loss Induced by O<sub>3</sub> Exposure

Figure 2 illustrates NPP changes across various ecosystems in the 95–100% range as O<sub>3</sub> exposure increases. In forest ecosystems (Figure 2a), NPP rises significantly at O<sub>3</sub> concentrations of 20,000 to 32,118  $\mu\text{g m}^{-3} \text{ yr}^{-1}$  (slope =  $0.1 \text{ gC}/\mu\text{g m}^{-3} \text{ yr}^{-1}$ ,  $R^2 = 0.95$ ,  $p = 2.59 \times 10^{-32}$ ). Above 32,118  $\mu\text{g m}^{-3} \text{ yr}^{-1}$ , NPP declines (slope =  $-0.11 \text{ gC}/\mu\text{g m}^{-3} \text{ yr}^{-1}$ ,  $R^2 = 0.98$ ,  $p = 2.29 \times 10^{-42}$ ). Shrubs (Figure 2b) show a similar trend, with significant NPP increases at 20,000 to 32,074  $\mu\text{g m}^{-3} \text{ yr}^{-1}$  (slope =  $0.1 \text{ gC}/\mu\text{g m}^{-3} \text{ yr}^{-1}$ ,  $R^2 = 0.95$ ,  $p = 1.49 \times 10^{-32}$ ). Above this concentration, NPP decreases (slope =  $-0.09 \text{ gC}/\mu\text{g m}^{-3} \text{ yr}^{-1}$ ,  $R^2 = 0.98$ ,  $p = 6.05 \times 10^{-43}$ ). Grass ecosystems (Figure 2c) experience significant NPP growth between 20,000 and 28,324  $\mu\text{g m}^{-3} \text{ yr}^{-1}$  (slope =  $0.05 \text{ gC}/\mu\text{g m}^{-3} \text{ yr}^{-1}$ ,  $R^2 = 0.75$ ,  $p = 1.05 \times 10^{-15}$ ), followed by a decline at higher concentrations (slope =  $-0.03 \text{ gC}/\mu\text{g m}^{-3} \text{ yr}^{-1}$ ,  $R^2 = 0.93$ ,  $p = 8.44 \times 10^{-30}$ ). Crop (Figure 2d) also shows increased NPP at 20,000 to 31,728  $\mu\text{g m}^{-3} \text{ yr}^{-1}$  (slope =  $0.06 \text{ gC}/\mu\text{g m}^{-3} \text{ yr}^{-1}$ ,  $R^2 = 0.91$ ,  $p = 1.02 \times 10^{-26}$ ) but decreases significantly at levels above 31,728  $\mu\text{g m}^{-3} \text{ yr}^{-1}$  (slope =  $-0.05 \text{ gC}/\mu\text{g m}^{-3} \text{ yr}^{-1}$ ,  $R^2 = 0.98$ ,  $p = 2.38 \times 10^{-30}$ ).

Additionally, Figure S2 depicts NPP changes within the 48–52% range. All ecosystems—forest (Figure S2a), shrub (Figure S2b), grass (Figure S2c), and crop (Figure S2d)—exhibit a similar pattern: NPP increases initially and then decreases when O<sub>3</sub> exposure exceeds a certain threshold, indicating potential loss across ecosystems.

Regarding model fit: In the high-percentile (95–100%) analyses,  $R^2$  values range from 0.75 to 0.98, indicating strong explanatory power. In the medium-percentile (48–52%) analyses (Figure S2), some segments have lower  $R^2$  values (minimum  $\sim 0.35$ ). This does not undermine our main conclusions because the primary purpose of segmented regression is to detect the turning point (change in slope direction) rather than to build a high-precision predictive model. The consistency of the slope-direction change across percentiles and ecosystems provides strong evidence for the threshold response. Moreover, in Supplementary Figure S5, we compare linear, quadratic, segmented linear, and segmented nonlinear models; the segmented linear model consistently outperforms the others (adjusted  $R^2$ ), statistically supporting the existence of a threshold.

#### Remote Sensing Evidence of NPP Loss Induced by NO<sub>2</sub> Exposure

Using the method from the section titled Remote sensing evidence of NPP loss induced by O<sub>3</sub> exposure, we investigated remote sensing evidence of NPP loss due to NO<sub>2</sub> exposure. Figure 3 shows NPP changes across ecosystems in the 95–100% range as NO<sub>2</sub> levels increase. Forests (Figure 3a) experience significant NPP growth at NO<sub>2</sub> concentrations of 4000 to 4968  $\mu\text{g m}^{-3} \text{ yr}^{-1}$  (slope =  $0.44 \text{ gC}/\mu\text{g m}^{-3} \text{ yr}^{-1}$ ,  $R^2 = 0.93$ ,  $p = 4.68 \times 10^{-4}$ ). Above 4968  $\mu\text{g m}^{-3} \text{ yr}^{-1}$ , NPP decreases significantly (slope =  $-0.08 \text{ gC}/\mu\text{g m}^{-3} \text{ yr}^{-1}$ ,  $R^2 = 0.83$ ,  $p = 2.43 \times 10^{-31}$ ). Shrub (Figure 3b) shows significant NPP increases at 4000 to 4890  $\mu\text{g m}^{-3} \text{ yr}^{-1}$  (slope =  $0.28 \text{ gC}/\mu\text{g m}^{-3} \text{ yr}^{-1}$ ,  $R^2 = 0.98$ ,  $p = 1.69 \times 10^{-4}$ ), followed by a decrease

above this concentration (slope =  $-0.10 \text{ gC}/\mu\text{g m}^{-3} \text{ yr}^{-1}$ ,  $R^2 = 0.85$ ,  $p = 1.79 \times 10^{-27}$ ). Grass (Figure 3c) shows significant NPP increases between 4000 and 3646  $\mu\text{g m}^{-3} \text{ yr}^{-1}$  (slope =  $0.10 \text{ gC}/\mu\text{g m}^{-3} \text{ yr}^{-1}$ ,  $R^2 = 0.65$ ,  $p = 5.18 \times 10^{-2}$ ), but declines at higher levels (slope =  $-0.02 \text{ gC}/\mu\text{g m}^{-3} \text{ yr}^{-1}$ ,  $R^2 = 0.85$ ,  $p = 1.42 \times 10^{-28}$ ). Crop (Figure 3d) also experiences increased NPP at 4000 to 4797  $\mu\text{g m}^{-3} \text{ yr}^{-1}$  (slope =  $0.22 \text{ gC}/\mu\text{g m}^{-3} \text{ yr}^{-1}$ ,  $R^2 = 0.81$ ,  $p = 1.46 \times 10^{-2}$ ), but decreases significantly above this concentration (slope =  $-0.05 \text{ gC}/\mu\text{g m}^{-3} \text{ yr}^{-1}$ ,  $R^2 = 0.79$ ,  $p = 9.48 \times 10^{-24}$ ). Figure S3 illustrates NPP changes in the 48–52% range, showing a similar pattern of initial increase followed by a decrease across all ecosystems. This indicates that NPP loss occurs when  $\text{NO}_2$  exposure exceeds certain thresholds.

In summary, the remote sensing evidence of NPP loss under combined  $\text{NO}_2$  and  $\text{O}_3$  exposure, detailed in the sections titled Remote Sensing Evidence of NPP Loss Induced by  $\text{O}_3$  Exposure and Remote Sensing Evidence of NPP Loss Induced by  $\text{NO}_2$  Exposure, clearly shows that China's terrestrial ecosystems' NPP is jointly influenced by these pollutants.

### 3.2.2. Determination of NPP Loss Threshold

We analyzed scatter plots of NPP versus  $\text{O}_3$  and  $\text{NO}_2$  exposure for forest, shrub, grass, and crop ecosystems from 2008 to 2021. We observed large and small NPP clusters within these point pairs. To detect changes in ecosystem NPP in response to increasing pollutant concentrations, we employed K-means clustering analysis on the 95–100% and 48–52% histograms. From the response curves in Figures 2, 3, S2 and S3, we extracted threshold values for NPP loss inflection points for different ecosystem types (see Table 1).

**Table 1.** Thresholds for NPP Loss in different ecosystem types under  $\text{O}_3$  and  $\text{NO}_2$  exposure.

|        | Large NPP (95–100%) |                                      |               |                                       | Small NPP (48–52%) |                                      |               |                                       |
|--------|---------------------|--------------------------------------|---------------|---------------------------------------|--------------------|--------------------------------------|---------------|---------------------------------------|
|        | $\text{O}_3$        | $\text{NPP}_{\text{max},\text{O}_3}$ | $\text{NO}_2$ | $\text{NPP}_{\text{max},\text{NO}_2}$ | $\text{O}_3$       | $\text{NPP}_{\text{max},\text{O}_3}$ | $\text{NO}_2$ | $\text{NPP}_{\text{max},\text{NO}_2}$ |
| Forest | 32,118              | 1579                                 | 4968          | 1598                                  | 34,391             | 759                                  | 4828          | 762                                   |
| Shrub  | 32,074              | 1493                                 | 4890          | 1463                                  | 31,806             | 771                                  | 4718          | 812                                   |
| Grass  | 28,324              | 836                                  | 3646          | 833                                   | 28,056             | 526                                  | 3484          | 494                                   |
| Crop   | 31,728              | 1129                                 | 4797          | 1266                                  | 30,637             | 517                                  | 5124          | 499                                   |

The units of  $\text{O}_3$  and  $\text{NO}_2$  are  $\mu\text{g m}^{-3} \text{ yr}^{-1}$ ,  $\text{g C}/\text{m}^2$  for NPP.

Table 1 reveals that forests, shrubs, and crops require higher  $\text{O}_3$  and  $\text{NO}_2$  exposure for NPP loss, while grass exhibits lower thresholds for both pollutants. The  $\text{O}_3$  and  $\text{NO}_2$  thresholds for NPP loss in forest and shrub ecosystems are similar, with  $\text{NO}_2$  thresholds being lower than those for  $\text{O}_3$ . Grass ecosystems are more susceptible to NPP inhibition from  $\text{O}_3$  and  $\text{NO}_2$  exposure compared to forests, shrubs, and crops. Table S3 presents the percentile values of the  $\text{O}_3$  and  $\text{NO}_2$  exposure dose thresholds, further indicating that  $\text{NO}_2$  exposure is more likely than  $\text{O}_3$  exposure to cause NPP loss in ecosystems.

### 3.2.3. Establishment of the NPP Loss Model

Using results from Sections 3.2.1 and 3.2.2, we developed response equations for NPP in forest, shrub, grass, and crop ecosystems relative to  $\text{O}_3$  and  $\text{NO}_2$  exposure. To better analyze pollutant impacts on NPP loss, we categorized NPP within each ecosystem into large and small types based on scatter plot distribution.

#### a. Large NPP ecosystem type

The equation influenced by O<sub>3</sub> only is as follows:

$$\begin{aligned} NPP_{obs,i} &\geq NPP_{threshold,i} \\ c_{O_3,i} &\geq c_{O_3,threshold,i} \cup c_{NO_2,i} < c_{NO_2,threshold,i} \\ y_{h,NPP,O_3,i} &= a_{h,1,i} \cdot c_{O_3,i} + b_{h,1,i} \\ Loss_{h,O_3,i} &= (NPP_{obs,i} / y_{h,NPP,O_3,i} - 1) \cdot 100\% \end{aligned} \quad (1)$$

The equation influenced by NO<sub>2</sub> only is as follows:

$$\begin{aligned} NPP_{obs,i} &\geq NPP_{threshold,i} \\ c_{O_3,i} < c_{O_3,threshold,i} \cup c_{NO_2,i} &\geq c_{NO_2,threshold,i} \\ y_{h,NPP,NO_2,i} &= a_{h,2,i} \cdot c_{NO_2,i} + b_{h,2,i} \\ Loss_{h,NO_2,i} &= (NPP_{obs,i} / y_{h,NPP,NO_2,i} - 1) \cdot 100\% \end{aligned} \quad (2)$$

The equation influenced by both O<sub>3</sub> and NO<sub>2</sub> is as follows:

$$\begin{aligned} NPP_{obs,i} &\geq NPP_{threshold,i} \\ c_{O_3,i} < c_{O_3,threshold,i} \cup c_{NO_2,i} &\geq c_{NO_2,threshold,i} \\ y_{h,NPP,O_3,i} &= a_{h,1,i} \cdot c_{O_3,i} + b_{h,1,i} \\ y_{h,NPP,NO_2,i} &= a_{h,2,i} \cdot c_{NO_2,i} + b_{h,2,i} \\ Loss_{h,O_3,NO_2,i} &= (2 \cdot NPP_{obs,i} / (y_{h,NPP,O_3,i} + y_{h,NPP,NO_2,i}) - 1) \cdot 100\% \end{aligned} \quad (3)$$

#### b. Small NPP ecosystem type

The equation influenced by O<sub>3</sub> only is as follows:

$$\begin{aligned} NPP_{obs,i} &< NPP_{threshold,i} \\ c_{O_3,i} &\geq c_{O_3,threshold,i} \cup c_{NO_2,i} < c_{NO_2,threshold,i} \\ y_{l,NPP,O_3,i} &= a_{l,1,i} \cdot c_{O_3,i} + b_{l,1,i} \\ Loss_{O_3,i} &= (NPP_{obs,i} / y_{l,NPP,O_3,i} - 1) \cdot 100\% \end{aligned} \quad (4)$$

The equation influenced by NO<sub>2</sub> only is as follows:

$$\begin{aligned} NPP_{obs,i} &< NPP_{threshold,i} \\ c_{O_3,i} < c_{O_3,threshold,i} \cup c_{NO_2,i} &\geq c_{NO_2,threshold,i} \\ y_{l,NPP,NO_2,i} &= a_{l,2,i} \cdot c_{NO_2,i} + b_{l,2,i} \\ Loss_{l,NO_2,i} &= (NPP_{obs,i} / y_{l,NPP,NO_2,i} - 1) \cdot 100\% \end{aligned} \quad (5)$$

The equation influenced by both O<sub>3</sub> and NO<sub>2</sub> is as follows:

$$\begin{aligned} NPP_{obs,i} &< NPP_{threshold,i} \\ c_{O_3,i} < c_{O_3,threshold,i} \cup c_{NO_2,i} &\geq c_{NO_2,threshold,i} \\ y_{l,NPP,O_3,i} &= a_{l,1,i} \cdot c_{O_3,i} + b_{l,1,i} \\ y_{l,NPP,NO_2,i} &= a_{l,2,i} \cdot c_{NO_2,i} + b_{l,2,i} \\ Loss_{l,O_3,NO_2,i} &= (2 \cdot NPP_{obs,i} / (y_{l,NPP,O_3,i} + y_{l,NPP,NO_2,i}) - 1) \cdot 100\% \end{aligned} \quad (6)$$

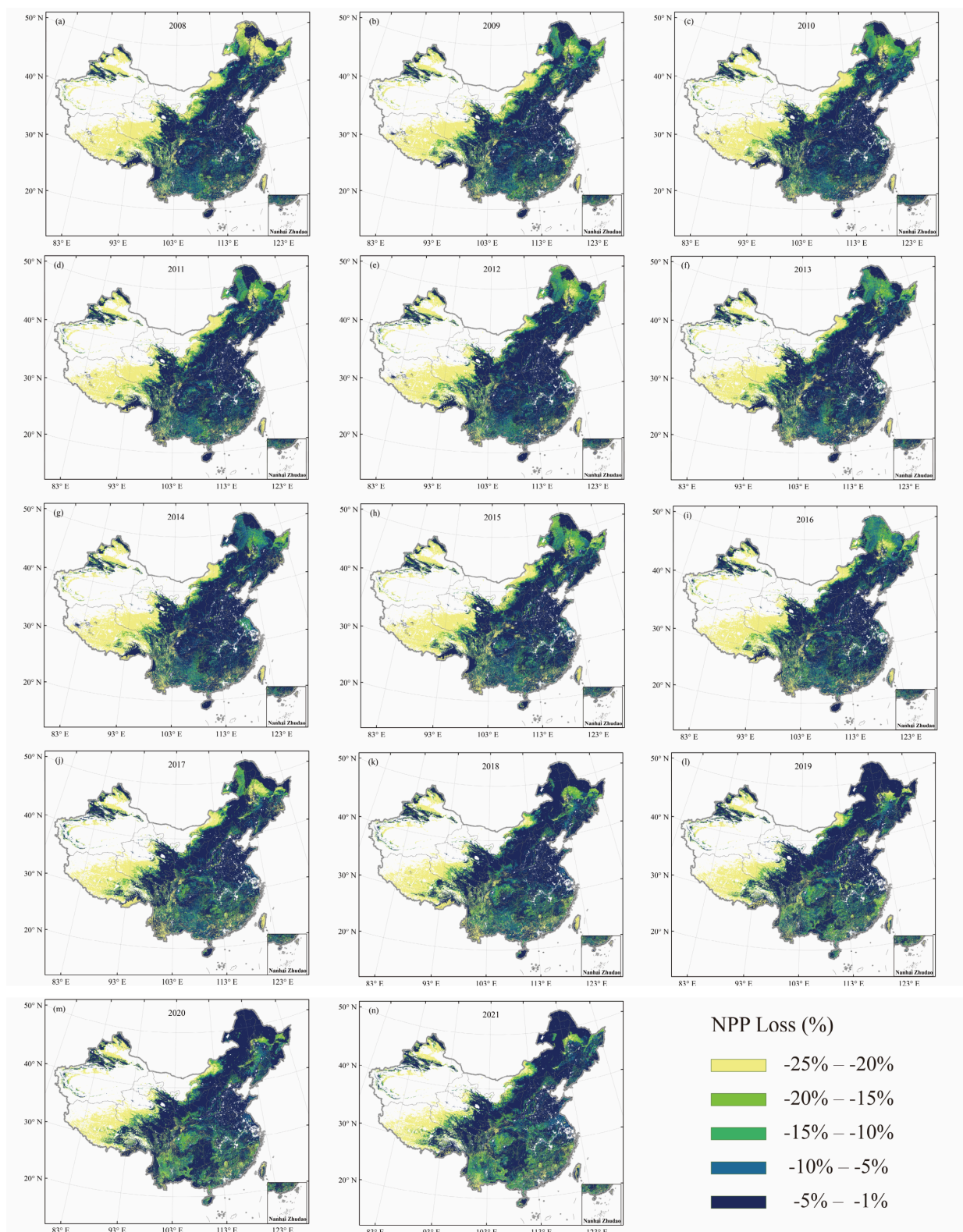
In Equations (1)–(6) above, NPP<sub>obs</sub> and NPP<sub>threshold</sub> refer to Modis NPP and the NPP loss threshold, respectively.

### 3.3. The Joint Pollutant Exposures Effect on NPP over China

#### 3.3.1. Spatial Patterns of NPP Loss from 2008 to 2021

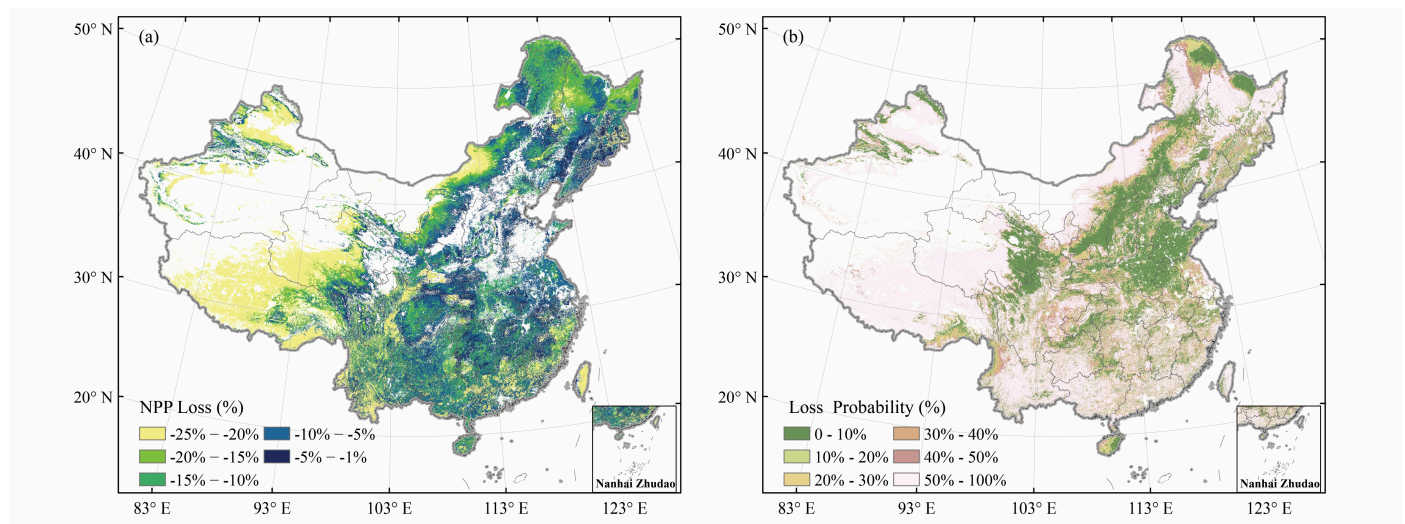
Using the NPP loss model from Section 3.2.3, we simulated the combined impact of O<sub>3</sub> and NO<sub>2</sub> pollution on NPP loss in China's terrestrial ecosystems from 2008 to 2021 (Figures 4 and 5). Figure 4 shows that, over the past 14 years, Northeast, North, Central,

and Southwest China experienced smaller NPP losses ( $-15\%$  to  $-1\%$ ), while Tibet and Xinjiang saw greater losses (over  $-15\%$ ).



**Figure 4.** The spatial distribution of annual NPP loss caused by combined  $O_3$  and  $NO_2$  pollution exposure from 2008 to 2021 (a–n). “Nanhai Zhudao” refers to the South China Sea Islands.





**Figure 5.** The multi-year average distribution of NPP loss in China's terrestrial ecosystems due to combined O<sub>3</sub> and NO<sub>2</sub> pollution exposure from 2008 to 2021 (a); (b) shows the probability of NPP loss occurring from 2008 to 2021, calculated as  $P_{Loss} = \frac{n_{NPP_{loss}}}{14} \cdot 100\%$ . Pixel-level loss probability is defined as the fraction of the 14 study years in which the modeled pollution-induced NPP loss is greater than zero for each individual pixel. "Nanhai Zhudao" refers to the South China Sea Islands.

Our framework reveals a clear spatial pattern of vulnerability (Figure 5a). From 2008 to 2021, the most severe NPP losses were consistently observed in the Tibetan Plateau and Northwest regions (west of 103° E), while eastern areas experienced smaller losses. The average NPP loss nationwide was approximately  $-17.4\% \pm 0.9\%$ . Figure 5b indicates that most regions in China had a high likelihood of NPP loss due to O<sub>3</sub> and NO<sub>2</sub> pollution, with an average loss probability of about 50.8%. Here, the pixel-level loss probability is explicitly defined as the fraction of the 14 study years in which the modeled pollution-induced NPP loss is greater than zero for each individual pixel. The regional average value of 50.8% represents the spatially averaged annual loss occurrence frequency across all pixels, rather than a statistical confidence level or significance probability. The Tibetan Plateau, Northwest, Southwest, Central, and Northeast regions had probabilities over 50%, while the North China Plain and eastern Gansu had lower probabilities (below 10%).

### 3.3.2. Annual Changes in NPP Loss Across Different Ecosystems

We conducted a statistical analysis of NPP loss in forest, shrub, grass, and crop ecosystems due to combined O<sub>3</sub> and NO<sub>2</sub> pollution from 2008 to 2021 (Figure 6). Forests experienced the largest NPP loss, while crops had the smallest. Grass showed the highest loss rate, followed by forest, both above the national average, while shrub and crop had lower rates. Forest (Figure 6a) had an average annual NPP loss of  $-0.30 \pm 0.05$  Pg C·yr<sup>-1</sup> (loss rate:  $-20.6\% \pm 2.4\%$ ), with a 14-year cumulative loss of  $-4.22$  Pg C. Shrub (Figure 6b) lost  $-0.15 \pm 0.01$  Pg C·yr<sup>-1</sup> (loss rate:  $-13.2\% \pm 0.6\%$ ), about half the loss of forests. Grass (Figure 6c) showed  $-0.14 \pm 0.01$  Pg C·yr<sup>-1</sup> (loss rate:  $-23.4\% \pm 1.3\%$ ). Crop (Figure 6d) had  $-0.08 \pm 0.01$  Pg C·yr<sup>-1</sup> (loss rate:  $-12.7\% \pm 1.0\%$ ). The national average NPP loss (Figure 6e) was  $-0.68 \pm 0.06$  Pg C·yr<sup>-1</sup> (loss rate:  $-17.5\% \pm 1.0\%$ ), totaling  $-9.48$  Pg C over 14 years—equivalent to 2.45 years of NPP. Losses in 2013, 2014, 2015, and 2017 were particularly high ( $-0.70$  to  $-0.76$  Pg C).





**Figure 6.** The annual variation in NPP loss for forest (a), shrub (b), grass (c), crop (d), and China's terrestrial ecosystems (e) from 2008 to 2021. In the figure, "Original" and "Estimated" represent

the MODIS satellite-observed NPP and the NPP loss estimated by the model, respectively. In (a), “ $-0.30 \pm 0.05$ ” indicates the mean total NPP loss  $\pm$  standard deviation, and “ $-20.6\% \pm 2.4\%$ ” represents the mean percentage of NPP loss  $\pm$  standard deviation (full-model final output). Note: Loss rates shown here are full-model final outputs; complementary threshold-sensitivity baseline diagnostic results are provided in Table S2.

## 4. Discussion

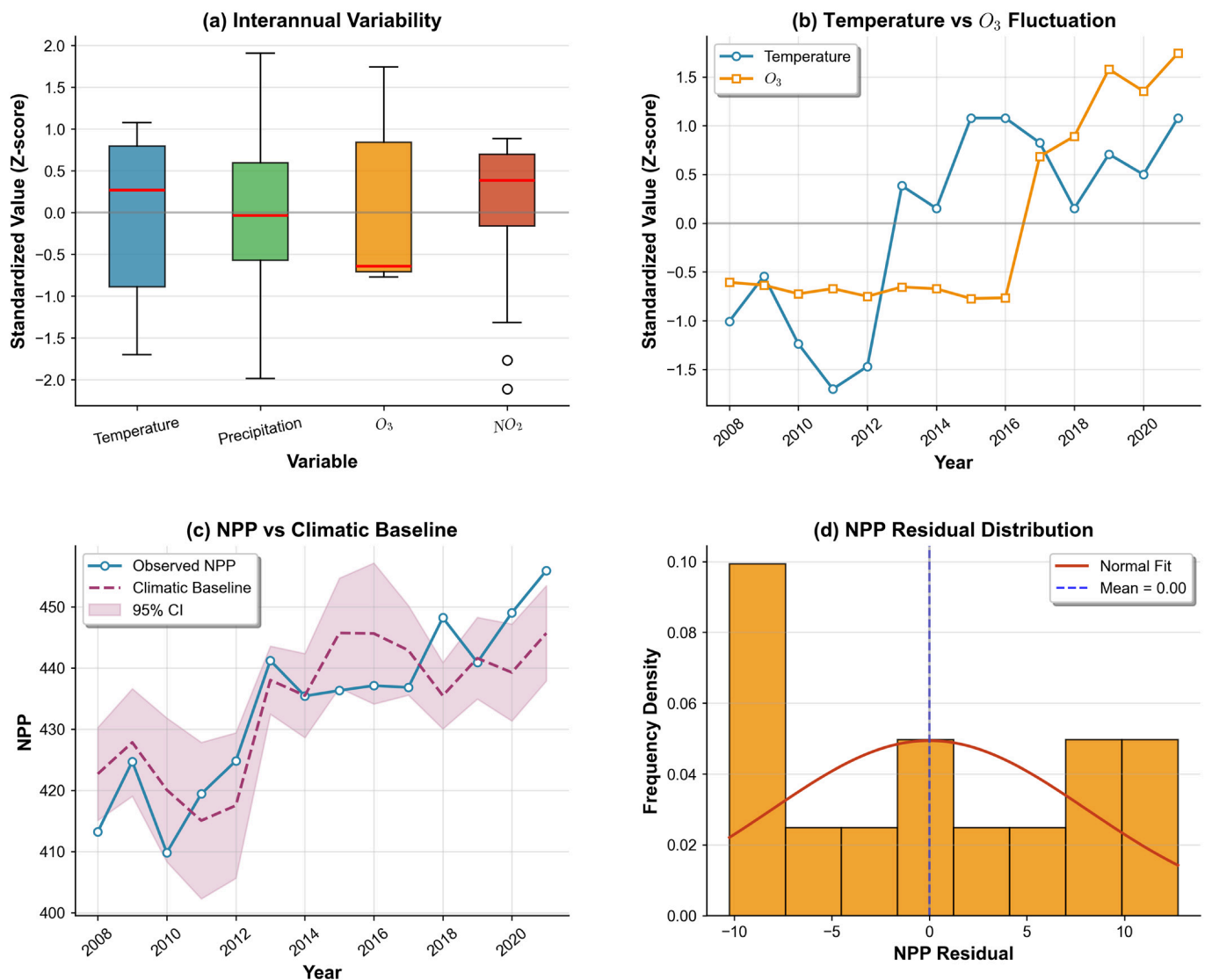
We interpret the key findings on nonlinear NPP responses to combined O<sub>3</sub> and NO<sub>2</sub> pollution, contextualize them within existing literature, discuss ecological and policy implications, address limitations, and outline future directions. By integrating empirical evidence from partial correlations, segmented models, and residual analyses, we demonstrate the combined regulation of NPP by stable climate baselines and episodic pollutant disturbances, providing robust support for our parsimonious framework.

### 4.1. Joint Regulation of NPP by Climate Baseline Rhythms and Pollutant Disturbances

Based on the 2008–2021 analysis of NPP, temperature, precipitation, O<sub>3</sub>, and NO<sub>2</sub> data across China’s ecosystems, our results indicate that spatiotemporal NPP variations are jointly regulated by stable climate baseline rhythms and episodic pollutant disturbances. This conclusion is empirically supported by key figures, clearly delineating the independent and interactive effects of each driver.

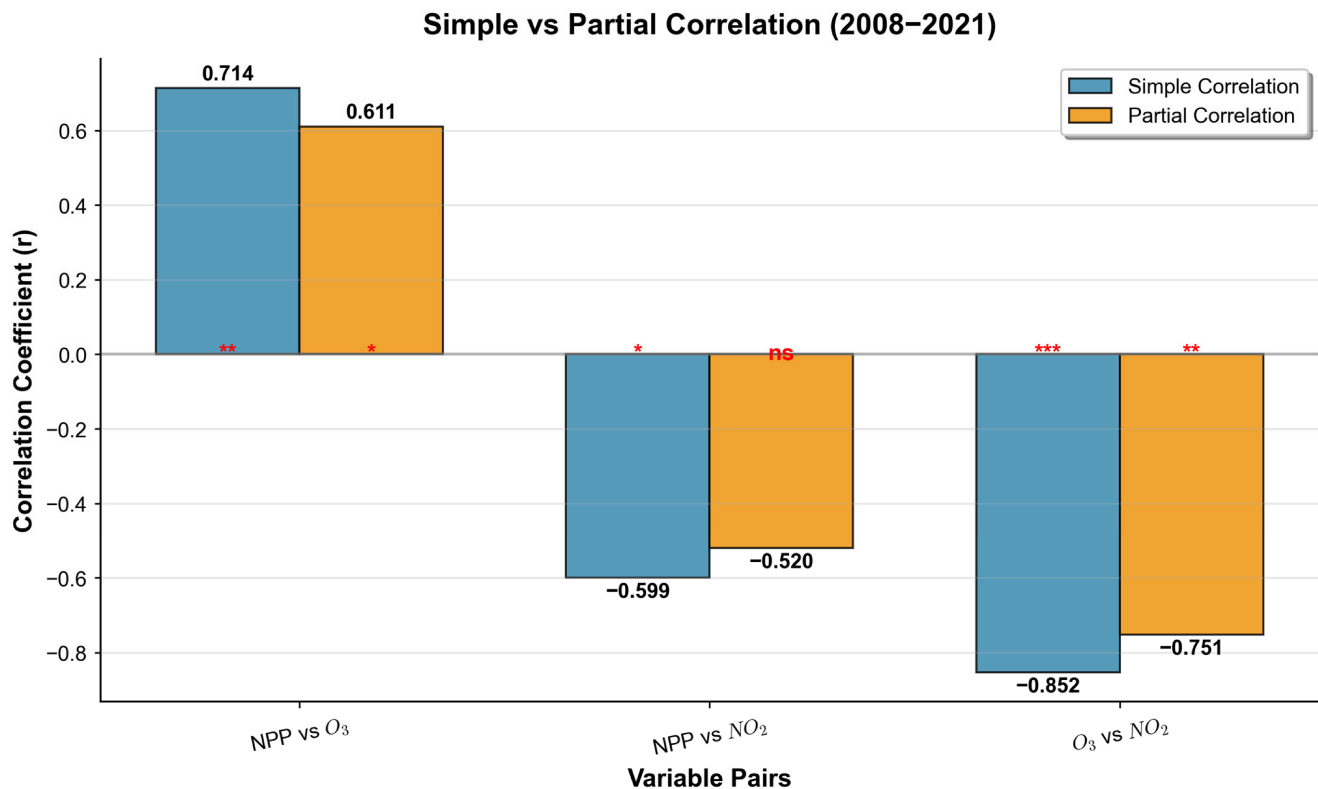
Climatic factors (temperature and precipitation) exhibit stable baseline driving characteristics, as directly evidenced by Figure 7. This figure integrates comparisons of observed NPP with climate-fitted baselines (temperature + precipitation), showing significant alignment between the two—with the 95% confidence interval encompassing most observations, visually confirming climate’s foundational role in shaping NPP. Figure 7 also includes standardized boxplots that reveal minimal fluctuation in climatic factors, with their average interannual coefficient of variation (CV) totaling only 5.59%, indicating low volatility and rhythmic stability. Together, temperature and precipitation explain 58.8% of NPP variance (adjusted  $R^2 = 0.588$  in the climate baseline model): temperature exerts a significant positive effect (coefficient = 25.6040,  $p = 0.002$ ), while precipitation’s direct effect is non-significant ( $p = 0.990$ ). Residual diagnostics validate model reliability (normality  $p = 0.229$ , homoscedasticity  $p = 0.931$ ), and no significant thresholds or nonlinearity were detected for climatic factors—further corroborating their role as stable baseline regulators of NPP.

In contrast, pollutants (O<sub>3</sub>, NO<sub>2</sub>) display “high volatility + differentiated impacts” as illustrated by the variability analyses integrated in Figure 7. The standardized boxplots for pollutants in this figure show markedly larger fluctuation amplitudes than those for climatic factors, with an average interannual CV of 9.09%—consistent with the core traits of episodic disturbances. Figure 8 (comparison of simple and partial correlations) uses bar charts to clarify the confounding effects of climate: the simple correlation between O<sub>3</sub> and NPP ( $r = 0.714$ ) exceeds the partial correlation ( $r = 0.611$ ,  $p < 0.05$ ), reflecting climate-induced confounding, while the partial correlation reveals a positive linear association between O<sub>3</sub> and NPP after accounting for climatic covariates. For NO<sub>2</sub> and NPP, the partial correlation ( $r = -0.520$ ,  $p = 0.0832$ ) weakens compared to the simple correlation ( $r = -0.599$ ), indicating that NO<sub>2</sub>’s impact is primarily mediated by climatic factors. Additionally, Figure 8 shows that O<sub>3</sub> and NO<sub>2</sub> remain strongly negatively correlated after controlling for climate and NPP ( $r = -0.751$ ,  $p < 0.05$ ), suggesting inherent co-emission or transformation relationships independent of the studied ecosystem drivers.



**Figure 7.** Interannual variability of climate-pollutant drivers and NPP residual characterization (2008–2021). **(a)** Standardized interannual variability of temperature, precipitation,  $O_3$ , and  $NO_2$  (Z-score normalization); the red line within each box indicates the median. **(b)** Temporal fluctuation alignment between standardized temperature and  $O_3$  concentrations. **(c)** Observed NPP versus climate-driven baseline (temperature + precipitation) with 95% confidence interval (CI). **(d)** Probability density distribution of NPP residuals (climatic baseline-corrected NPP anomalies).

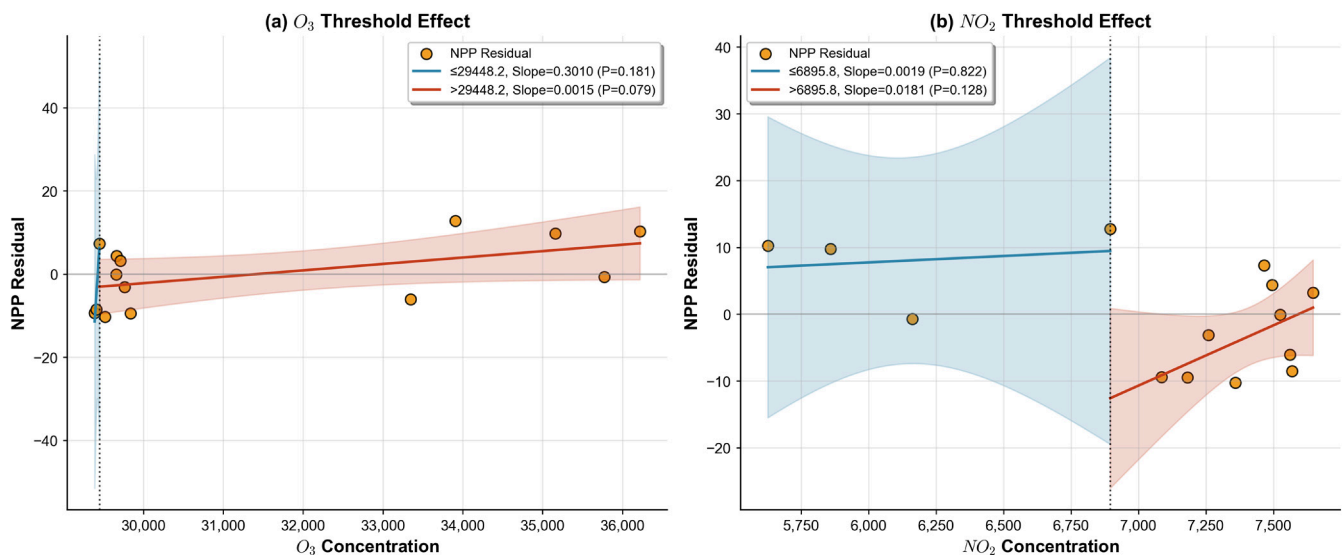
It is important to interpret these partial correlations with caution. They are computed on only 14 annual national means and thus cannot fully distinguish a genuine  $O_3$  effect from residual confounding by other trending variables (e.g., rising atmospheric  $CO_2$ , cumulative afforestation area, or non- $NO_2$  nitrogen deposition). Moreover, these linear partial-correlation results cannot capture the nonlinear threshold-dependent inhibitory effect of  $O_3$  highlighted in our main analysis. Therefore, we present these results as supportive evidence of association after removing linear climate effects, not as confirmation of causality.



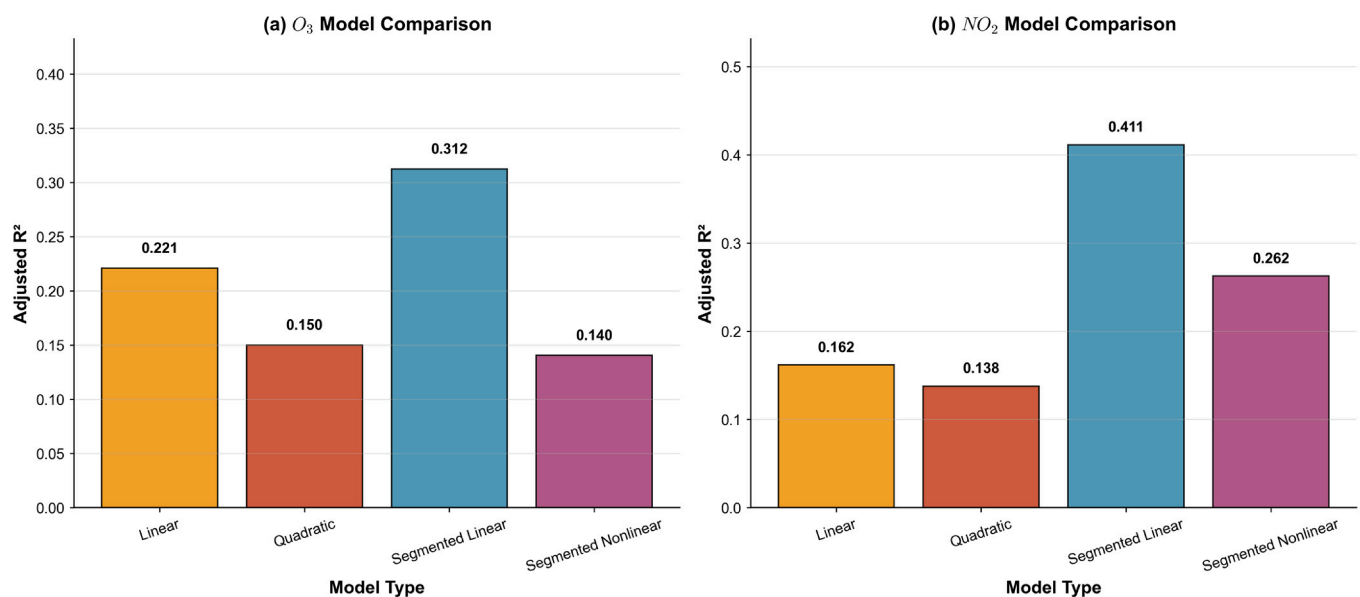
**Figure 8.** Comparison of simple and partial correlation coefficients for key variable pairs (2008–2021). Bar plot of Pearson’s  $r$  (simple correlation) and partial  $r$  (controlling for climatic/ecological covariates) for NPP- $O_3$ , NPP- $NO_2$ , and  $O_3$ - $NO_2$  pairs, with significance annotations (\*\* $p < 0.01$ , \*\*\*  $p < 0.001$ , \*  $p < 0.05$ , ns = not significant).

Segmented models further quantify pollutant thresholds, with Figures 9 and 10 ( $O_3$  and  $NO_2$  threshold effects, respectively) combining scatter plots, segmented regression lines, and 95% confidence bands to clearly identify turning points. For  $O_3$ , the optimal breakpoint is  $29,448.2 \mu\text{g m}^{-3} \text{ yr}^{-1}$ : the sub-threshold slope (0.3010) is steeper with better model fit (adjusted  $R^2 = 0.842$ ), while the post-threshold slope drops to 0.0015—corresponding to a 54.5% inhibition proportion in supplementary analyses.

For  $NO_2$ , the optimal breakpoint is  $6895.8 \mu\text{g m}^{-3} \text{ yr}^{-1}$ ; Figure 10 shows increased negative NPP residuals post-threshold, echoing a 70.0% inhibition rate (vs. 25.0% sub-threshold) and intensified inhibitory strength (6.70 vs. 0.69). Figure 11 (interannual variability statistics of key variables) complements these findings by quantifying the high volatility of pollutants relative to climate factors, while model fit comparisons (integrated in Figures 2 and 3) demonstrate the superiority of segmented linear models for capturing  $O_3$ -NPP (adjusted  $R^2 = 0.312$ ) and  $NO_2$ -NPP (adjusted  $R^2 = 0.411$ ) relationships over linear and quadratic models—visually validating the threshold-dependent effects of pollutants. Figure 4 further distinguishes inhibited from non-inhibited samples via bicolor scatter plots, highlighting strengthened post-threshold associations and confirming enhanced inhibitory trends.



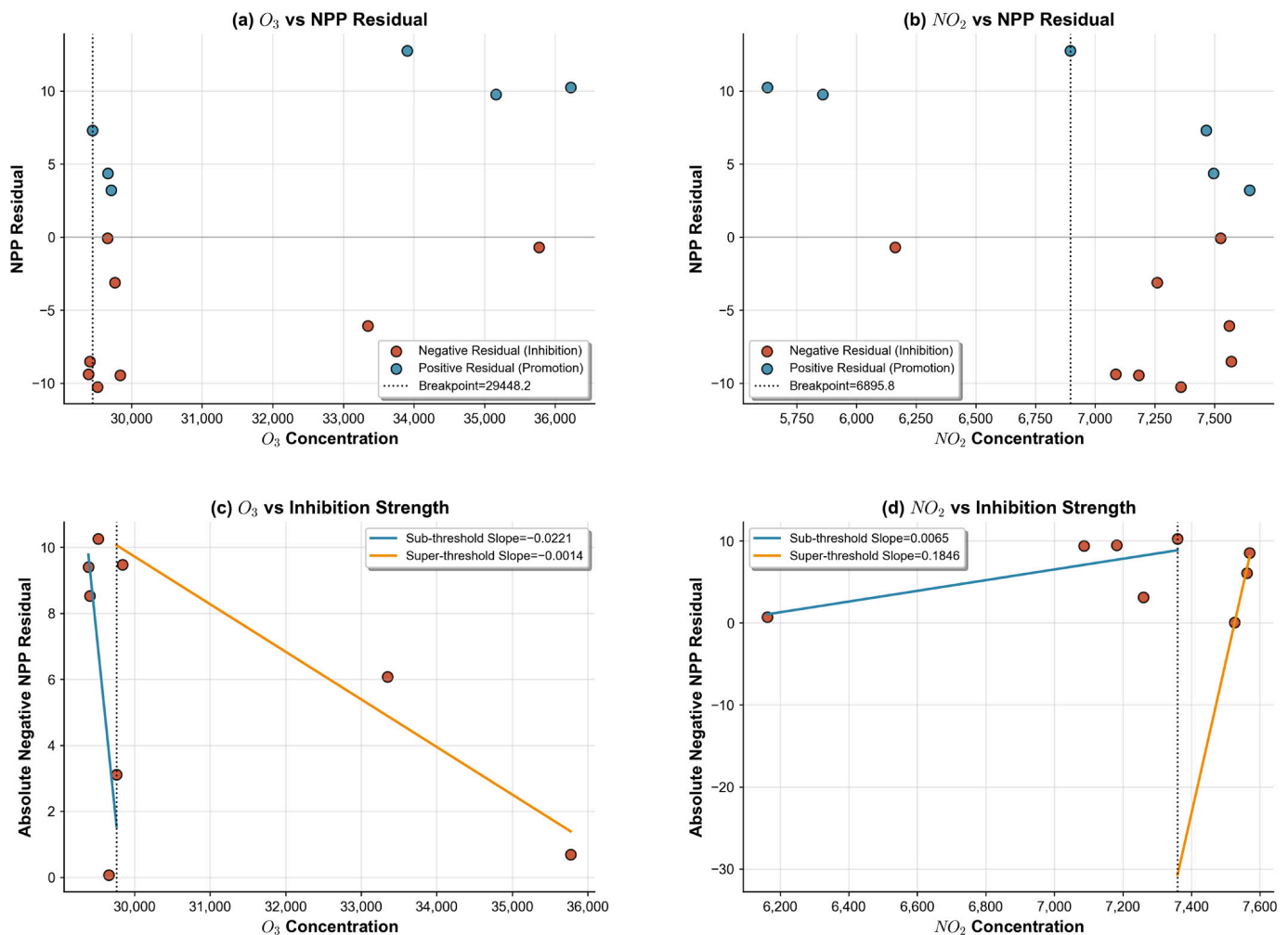
**Figure 9.** Threshold effects of  $O_3$  and  $NO_2$  concentrations on NPP residuals. (a) Segmented linear regression of  $O_3$  concentration versus NPP residuals, with optimal breakpoint and 95% CI for sub/super-threshold regimes. (b) Segmented linear regression of  $NO_2$  concentration versus NPP residuals, with optimal breakpoint and 95% CI for sub/super-threshold regimes.



**Figure 10.** Comparative performance of linear, quadratic, and segmented models for NPP residual-pollutant relationships. (a) Adjusted  $R^2$  of four model types (linear, quadratic, segmented linear, segmented nonlinear) for  $O_3$ -NPP residual fitting. (b) Adjusted  $R^2$  of four model types for  $NO_2$ -NPP residual fitting.

In summary, multiple lines of evidence from Figures 7–11 delineate the distinct roles of drivers in NPP variation: climatic factors construct the core spatiotemporal framework of NPP through low-volatility rhythms (evidenced by Figure 7), while  $O_3$  and  $NO_2$  impose superimposed disturbances via high volatility and threshold-dependent effects (supported by Figures 9–11). Key differentiations are the positive linear partial association for  $O_3$  and  $NO_2$ 's climate-mediated negative correlation, as quantified in Figure 8. These findings provide multidimensional empirical support for understanding ecosystem responses to concurrent climate change and air pollution, and support the scientific robustness of our method for extracting  $O_3$  and  $NO_2$  impacts on NPP from MODIS observations.





**Figure 11.** Inhibitory effects of  $O_3$  and  $NO_2$  on NPP: characterization of negative residuals. (a) Classification of NPP residuals (positive/promotion vs. negative/inhibition) against  $O_3$  concentrations, with optimal breakpoint. (b) Classification of NPP residuals against  $NO_2$  concentrations, with optimal breakpoint. (c) Segmented regression of  $O_3$  concentration versus absolute negative NPP residuals (inhibition strength). (d) Segmented regression of  $NO_2$  concentration versus absolute negative NPP residuals (inhibition strength).

#### 4.2. Comparison with Prior Studies

Our estimated thresholds ( $O_3$ : 28,324–34,391  $\mu\text{g m}^{-3} \text{yr}^{-1}$ ;  $NO_2$ : 3646–4968  $\mu\text{g m}^{-3} \text{yr}^{-1}$ ) align closely with field experiments, such as  $O_3$  critical levels of  $\sim 20,000$ – $30,000 \mu\text{g m}^{-3} \text{yr}^{-1}$  for forests [17,32] and  $NO_2$  inhibition thresholds of  $\sim 3000$ – $5000 \mu\text{g m}^{-3} \text{yr}^{-1}$  [28]. The cumulative loss of  $-9.48 \text{ Pg C}$  over 14 years ( $\sim 0.68 \text{ Pg C yr}^{-1}$ ) within the middle-to-high end of the range reported by Yue et al. [17] for  $O_3$  alone ( $\sim 0.5$ – $0.8 \text{ Pg C yr}^{-1}$ ). Our decomposition suggests  $NO_2$  may account for a moderate additional fraction of the total carbon loss, such that our combined pollutant estimate falls toward the upper end of the single-pollutant  $O_3$ -induced loss range reported by Yue et al. [17]. Compared to Lombardozzi et al. [15] global estimates scaled to China ( $\sim 1$ – $2 \text{ Pg C yr}^{-1}$ ), our estimate is lower, possibly due to methodological differences or the effectiveness of recent pollution controls. Partial correlations ( $O_3$ :  $r = 0.61$ ;  $NO_2$ :  $r = -0.52$ ) confirm pollutant effects independent of climate, extending prior single-pollutant models (e.g., [33]) by quantifying interactions ( $O_3$ – $NO_2$ :  $r = -0.75$ ).

The observed positive  $O_3$ –NPP correlation ( $r = 0.714$ ) at low exposures reflects hormesis-like responses [2,33], transitioning to inhibition beyond thresholds, consistent with Feng et al. [29] on oxidative stress amplification by  $NO_2$ .

#### 4.3. Ecological and Policy Implications

These findings highlight severe carbon sink erosion, with forests ( $-4.22$  Pg C cumulative loss) most vulnerable, equating to 2.45 years of China's terrestrial uptake. Spatial hotspots on the Tibetan Plateau and Northwest ( $>-15\%$  loss) underscore regional sensitivities, potentially exacerbating climate feedbacks [12].

The identified thresholds represent critical turning points where NPP shifts from weak stimulation to pronounced inhibition under increasing  $O_3$  and  $NO_2$  exposure. Ecologically, these thresholds indicate the pollutant exposure level at which terrestrial ecosystem carbon uptake begins to suffer substantial damage. We further compare our threshold magnitudes with values reported from prior experimental and modeling investigations. Despite discrepancies originating from ecosystem types, background environments and methodological differences, our thresholds fall within a reasonable range relative to published evidence.

Ecologically, combined  $O_3$ - $NO_2$  effects impair photosynthesis and nitrogen cycling [30], with high-volatility disturbances ( $CV = 9.09\%$ ) overlaying stable climate rhythms ( $CV = 5.59\%$ ). Policy-wise, integrated controls are urgent for carbon neutrality and the SDGs (13: Climate Action; 15: Life on Land), targeting hotspots via emission reductions.

#### 4.4. Limitations

First, this study suffers from inherent data-derived uncertainties and incomplete environmental constraint representation. The neglect of low- $NO_2$  fertilization effects may overestimate pollutant-driven NPP reduction with a documented bias of 5–15% [28], while unmeasured disturbances including drought and pests cannot be fully excluded, despite partial mitigation via multi-year data aggregation. In addition, MODIS cloud artifacts and CHAP fusion errors introduce systematic biases in high-elevation areas, and seasonal variability in  $O_3$  impacts further brings  $\pm 8\%$  sensitivity fluctuations in threshold estimation. Combined with intrinsic retrieval errors in satellite and reanalysis datasets, these multi-source data limitations induce unavoidable uncertainties in the final NPP loss quantification.

Second, mutual confounding between  $O_3$  and  $NO_2$  and sample size constraints limit the dissection of pollutant interactive effects. Consistent with atmospheric chemical mechanisms, the two pollutants exhibit strong covariation, and their independent and interactive impacts cannot be fully disentangled in the current framework. Limited by the dataset sample size, joint multivariate segmented modeling is statistically infeasible due to excessive parameterization, thereby forcing the adoption of separate piecewise regression. This separate analytical scheme fails to capture genuine combined or non-additive joint effects, restricting the accuracy of compound pollutant impact assessment.

Third, statistical inference and computational methods contain notable methodological limitations. The grid-based spatial structure of the original data causes spatial autocorrelation and pseudo-replication, which inflates statistical significance and renders regression  $p$ -values non-rigorous for causal inference. Moreover, the current compound-pollutant loss estimation relies on simple arithmetic averaging of single-pollutant counterfactual outputs rather than a standardized bivariate joint-effect model. Pixel-level discrepancies between  $O_3$ -only and  $NO_2$ -only simulations further propagate uncertainties, indicating that the combined loss metric is only an approximate composite index rather than a precise quantification of joint pollutant effects.

Fourth, incomplete climate confounding adjustment and the observational nature of the study restrict causal attribution credibility. This study only controls for temperature and precipitation, ignoring critical NPP drivers including solar radiation, vapor pressure deficit, soil moisture, terrain elevation and drought events. Residual environmental heterogeneity within ecosystem stratification groups further retains uneliminated confounding biases.

Consequently, the detected nonlinear relationships between pollutants and NPP represent only statistical associations, not definitive causal effects, and the quantified loss estimates should be interpreted with caution rather than as deterministic pollutant-induced impacts.

#### 4.5. Future Directions

Future research can advance the present findings through multiple optimized analytical strategies. First, process-based ecological models (e.g., AVIM2, CLM) can be integrated with the pollutant response thresholds identified in this study to realize mechanistic validation of pollutant-NPP relationships, combined with Representative Concentration Pathway (RCP) scenario projections and in situ ground experimental verification. Specifically, dedicated interactive models incorporating  $O_3 \times NO_2$  interaction terms are urgently needed to identify the genuine combined effects of the two pollutants beyond simple additive effects. Furthermore, incorporating total nitrogen deposition and climate feedback mechanisms into the analytical framework will refine pollutant impact estimation results, providing more scientific support for the formulation of targeted ecosystem adaptation and resilience enhancement policies.

### 5. Conclusions

This study reveals threshold responses of terrestrial ecosystem carbon uptake to long-term  $O_3$  and  $NO_2$  co-exposure in China, leveraging high-resolution remote sensing data from 2008 to 2021. By integrating CHAP pollutant datasets with MODIS NPP and LUCC classifications, we quantified nonlinear NPP declines across forest, shrub, grass, and crop ecosystems. Key findings include strong correlations between NPP and exposures ( $O_3$ :  $r = 0.714$ ;  $NO_2$ :  $r = -0.599$ ), with initial low-dose enhancements transitioning to reductions beyond ecosystem-specific thresholds (e.g.,  $O_3$ : 28,324–34,391  $\mu g\ m^{-3}\ yr^{-1}$ ;  $NO_2$ : 3646–4968  $\mu g\ m^{-3}\ yr^{-1}$ ). High exposures drove NPP losses up to  $-43.9\%$  in grass, resulting in a national average annual loss of  $-17.4\%$  ( $-0.68\ Pg\ C\ yr^{-1}$ ) and a cumulative  $-9.48\ Pg\ C$  over 14 years—equivalent to 2.45 years of China's terrestrial NPP. Forests experienced the greatest cumulative loss ( $-4.22\ Pg\ C$ ), underscoring their vulnerability as primary carbon sinks.

These results highlight combined  $O_3$ - $NO_2$  threats, where  $NO_2$ 's dual role as an  $O_3$  precursor and nitrogen source intensifies oxidative stress, impairing photosynthesis and sequestration beyond additive effects. Spatially, losses were most severe in the Tibetan Plateau and Northwest ( $>-15\%$ ), with a 50.8% nationwide probability, driven by atmospheric and land-use factors. Our model, employing K-means clustering and segmented regression, addresses observational gaps, offering a scalable tool that outperforms single-pollutant analyses.

Ecologically, these findings indicate accelerated carbon cycle disruptions under climate change, amplifying warming feedbacks by eroding sinks comparable to major emissions. Policy-wise, they advocate integrated air quality management in vulnerable regions to advance China's carbon neutrality and SDGs (e.g., 13: Climate Action; 15: Life on Land). Limitations, such as unmodeled climate interactions and independent exposure assumptions, may underestimate synergies by 10–20%, warranting cautious extrapolation.

Future research should incorporate mechanistic models of pollutant–nitrogen–carbon interactions, validate thresholds with field experiments, and project RCP scenarios. Such advancements will bolster adaptive strategies, fostering resilient ecosystems amid escalating pollution. This work stresses the urgency of mitigation to preserve carbon sinks, promoting sustainable stewardship in a warming world.

In conclusion, by employing a purpose-built empirical framework, this study derives spatially explicit, observation-based metrics to address complex continental-scale ecological

questions. The approach offers a replicable template for large-scale ecosystem impact assessment and illustrates how methodological clarity, combined with strategic design, can help extract meaningful signals from continental-scale environmental data. While our analysis is subject to limitations including residual confounding from co-trending global drivers and the empirical nature of counterfactual decomposition, the findings highlight the urgent threat of combined air pollution to terrestrial carbon sinks and provide a useful observational benchmark for informing future monitoring and policy efforts in China.

**Supplementary Materials:** The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/atmos17080799/s1>. Figure S1: Annual variations in regional average NPP, O<sub>3</sub>, and NO<sub>2</sub> exposure in China from 2008 to 2021; Figure S2: The NPP variation curves for forest (a), shrub (b), grass (c), and crop (d) ecosystems within the 48–52% range of each O<sub>3</sub> pollution exposure bin. There are a total of 100 O<sub>3</sub> exposure bins. In the figure, the solid lines represent the segmented fitted lines, with green segments indicating the phase with no NPP loss and red segments indicating the phase with NPP loss. The intersection of the two lines represents the threshold point between NPP loss and no loss. The curves in the figure show the 14-year average results from 2008 to 2021. Binning was conducted year-by-year per ecosystem type; bin-level NPP values were averaged across 14-years to obtain composite response curves, on which segmented regression and threshold extraction were performed. Grey dashed lines denote threshold positions; Figure S3: The NPP variation curves for forest (a), shrub (b), grass (c), and crop (d) ecosystems within the 48–52% range of each NO<sub>2</sub> pollution exposure bin. There are a total of 100 NO<sub>2</sub> exposure bins. In the figure, the solid lines represent the segmented fitted lines, with green segments indicating the phase with no NPP loss and red segments indicating the phase with NPP loss. The intersection of the two lines represents the threshold point between NPP loss and no loss. The curves in the figure show the 14-year average results from 2008 to 2021. Binning was conducted year-by-year per ecosystem type; bin-level NPP values were averaged across 14-years to obtain composite response curves, on which segmented regression and threshold extraction were performed. Grey dashed lines denote threshold positions; Figure S4: The NPP variation curves for forest ecosystems for the 95–100% and 48–52% ranges within each O<sub>3</sub> (left panel) and NO<sub>2</sub> (right panel) pollution exposure bin. There are a total of 100 exposure bins. The figures are arranged in chronological order from 2008 to 2021; Figure S5: The NPP variation curves for shrub ecosystems for the 95–100% and 48–52% ranges within each O<sub>3</sub> (left panel) and NO<sub>2</sub> (right panel) pollution exposure bin. There are a total of 100 exposure bins. The figures are arranged in chronological order from 2008 to 2021; Figure S6: The NPP variation curves for grass ecosystems for the 95–100% and 48–52% ranges within each O<sub>3</sub> (left panel) and NO<sub>2</sub> (right panel) pollution exposure bin. There are a total of 100 exposure bins. The figures are arranged in chronological order from 2008 to 2021; Figure S7: The NPP variation curves for crop ecosystems for the 95–100% and 48–52% ranges within each O<sub>3</sub> (left panel) and NO<sub>2</sub> (right panel) pollution exposure bin. There are a total of 100 exposure bins. The figures are arranged in chronological order from 2008 to 2021; Table S1: Summary statistics of O<sub>3</sub> and NO<sub>2</sub> within each K-means-derived combined-pollution cluster (low, medium, high). For each pollutant, the three values denote the threshold boundaries separating low, medium, and high cumulative concentration regimes. Values labelled Low represent the upper bound of the low-concentration regime, Medium indicates the transition range, and High denotes the lower bound of the high-concentration regime for annual cumulative O<sub>3</sub> or NO<sub>2</sub> exposure; Table S2: Sensitivity Analyses for NPP Loss Estimates; Table S3: The percentile values of the exposure dose thresholds of O<sub>3</sub> and NO<sub>2</sub> in the histogram distribution corresponding to NPP loss in different ecosystems; Table S4: Coefficients of variation (CVs) of NPP, O<sub>3</sub>, NO<sub>2</sub>, temperature (T), and precipitation (P) for different ecosystem types at the pixel scale across China; Table S5: Performance comparison of alternative model specifications for O<sub>3</sub> and NO<sub>2</sub>.

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