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Supporting Information for

Mechanisms Driving Decadal Changes in the Carbonate System of a Coastal Plain Estuary

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Contents of this file

Figures S1 to S10
Captions for Figures S1 to S10
Table S1 to S2
Caption for Table S1 to S2

Introduction

This Supporting Information includes figures that provide additional details regarding the model forcing (section 2.3), model evaluation (section 3.1), comparisons between two datasets (section 3.2), model results (section 3.2), and discussions (section 4.1 and 4.2). Additionally, Table S2 includes comparisons between observed and modeled pH trends at 17 Water Quality Monitoring Program stations (https://datahub.chesapeakebay.net/) along the main channel of the Chesapeake Bay.

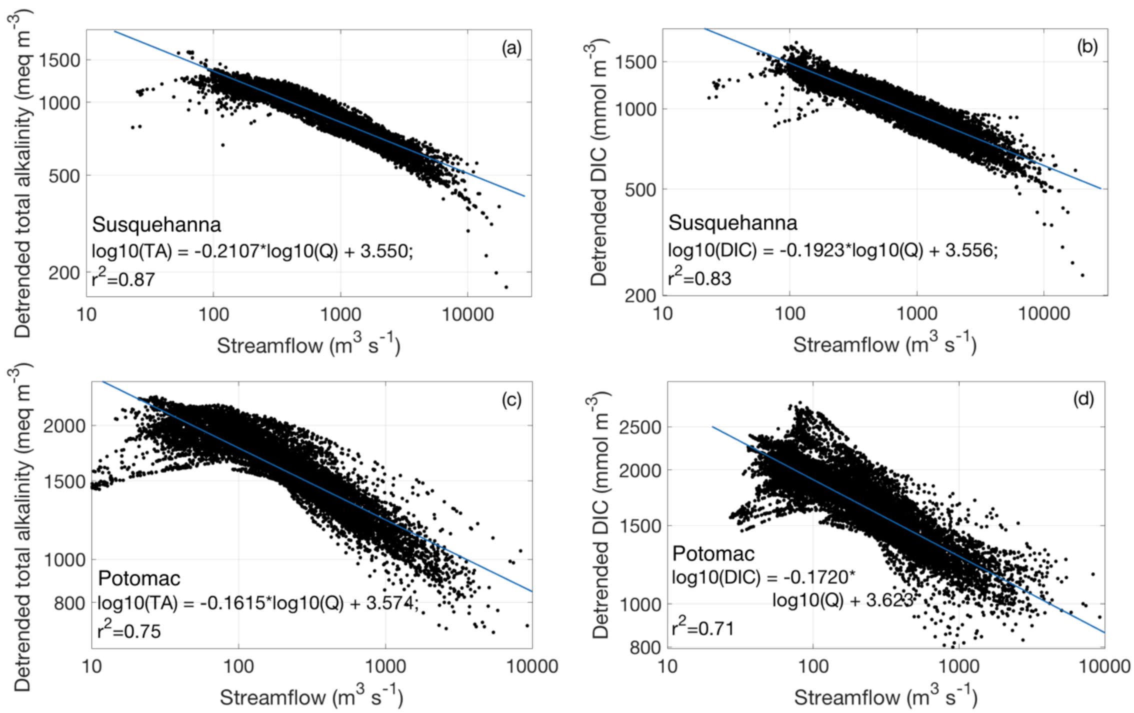

Figure S1. Discharge–TA and discharge–DIC relationships derived from long-term daily USGS data products for (a-b) the Susquehanna River (January 1985 to September 2016) and (c-d) the Potomac River (January 1985 to September 2013).

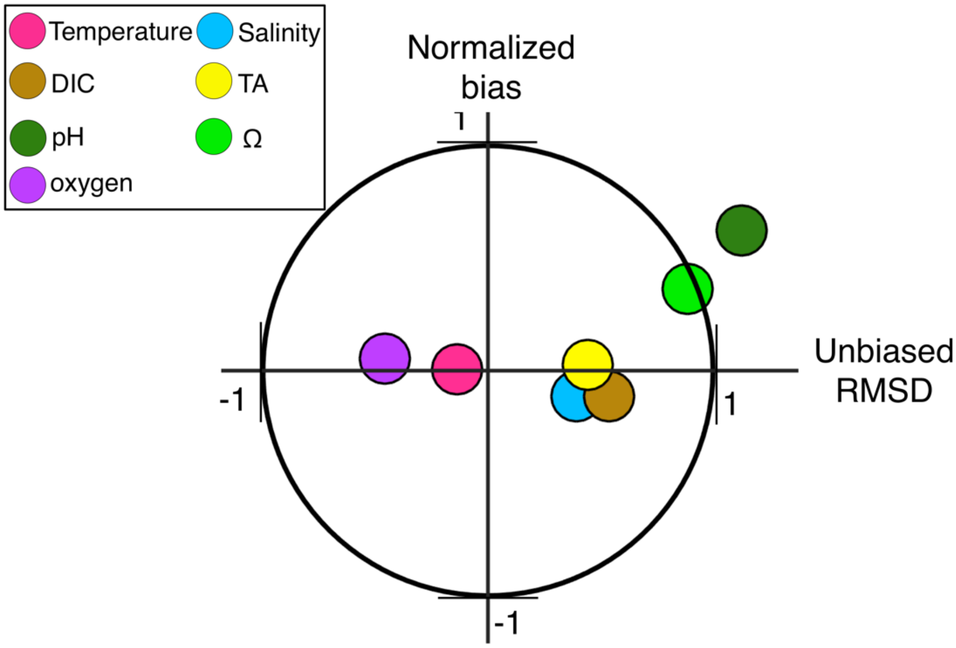

Figure S2. Target diagrams illustrating spatio-temporal model skill at 18 stations with recent carbonate system data sampled throughout the water column during 14 cruises from June 2016 to June 2018 (Friedman et al. 2020; see Figure 1 for station locations and section 2.1 for data details). Positive unbiased RMSD denotes that the standard deviation of the model results is greater than that of the observations. All skill metrics are normalized by the standard deviation of the observations.

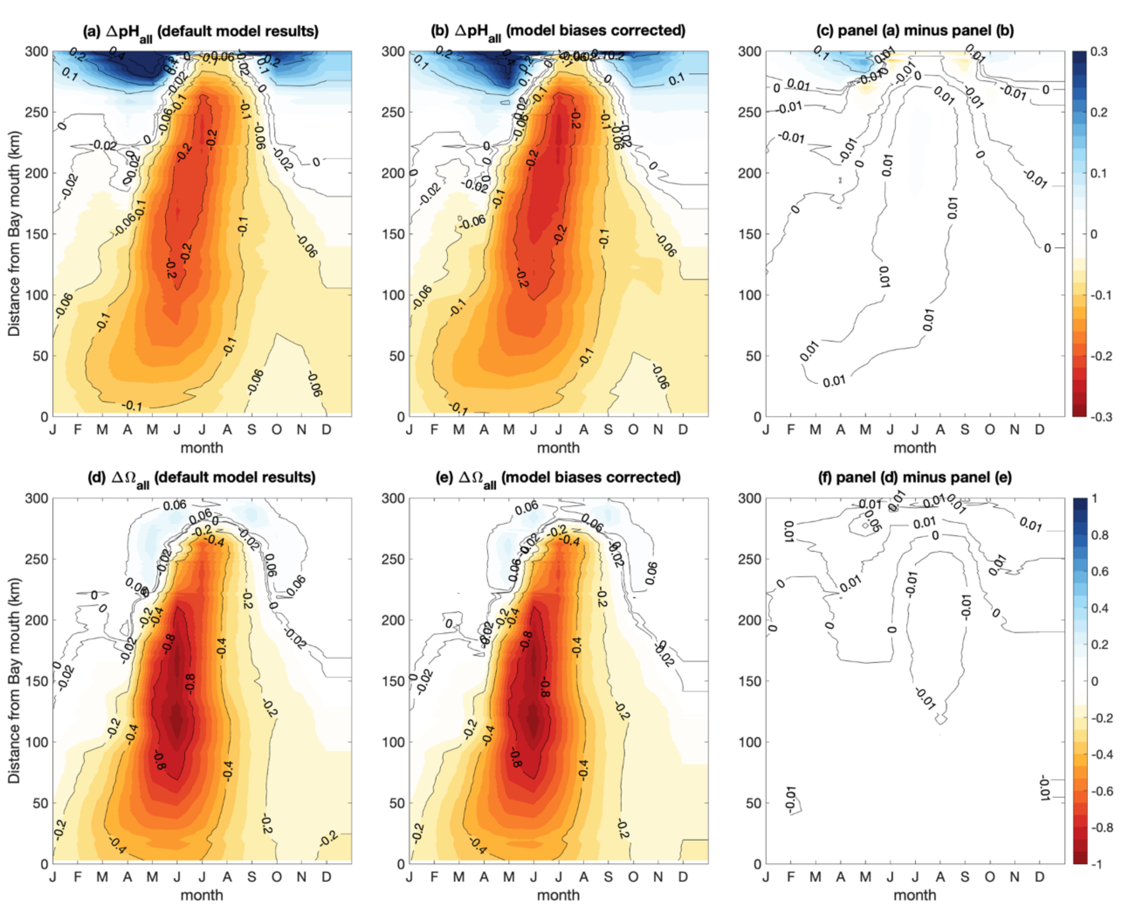

Figure S3. The impacts of overestimates in modeled pH and Ω_{AR} on the decadal trends computed in this study.

Note: The overestimates of pH and Ω_{AR} are due to the small positive bias in modeled TA and the small negative bias in modeled DIC (Table 1). Two sets of back-of-the-envelope calculations were conducted to quantify the impact of model biases on decadal pH and Ω_{AR} trends. In the first scenario, the 30-year changes in DIC and TA were applied to averaged model results from the Ref_{1985} simulation to calculate the 30-year changes in pH and Ω_{AR} (panel (a) and (d)). In the second scenario, the averaged model results were first corrected by the biases showed in Table 1 (i.e., –22.23 mmol m^{-3} and 5.41 meq m^{-3} for DIC and TA, respectively). Then, the same 30-year changes in DIC and TA were applied to the corrected model results to compute the 30-year changes in pH and Ω_{AR} (panel (b) and (e)). It is noteworthy that the 30-year changes in DIC and TA would have been different if the model had been perfect. Panel (c) and (f) show the difference between these two scenarios. Overall, the small underestimates in DIC and overestimates in TA have minimal impacts on the decadal trends in pH and Ω_{AR}.

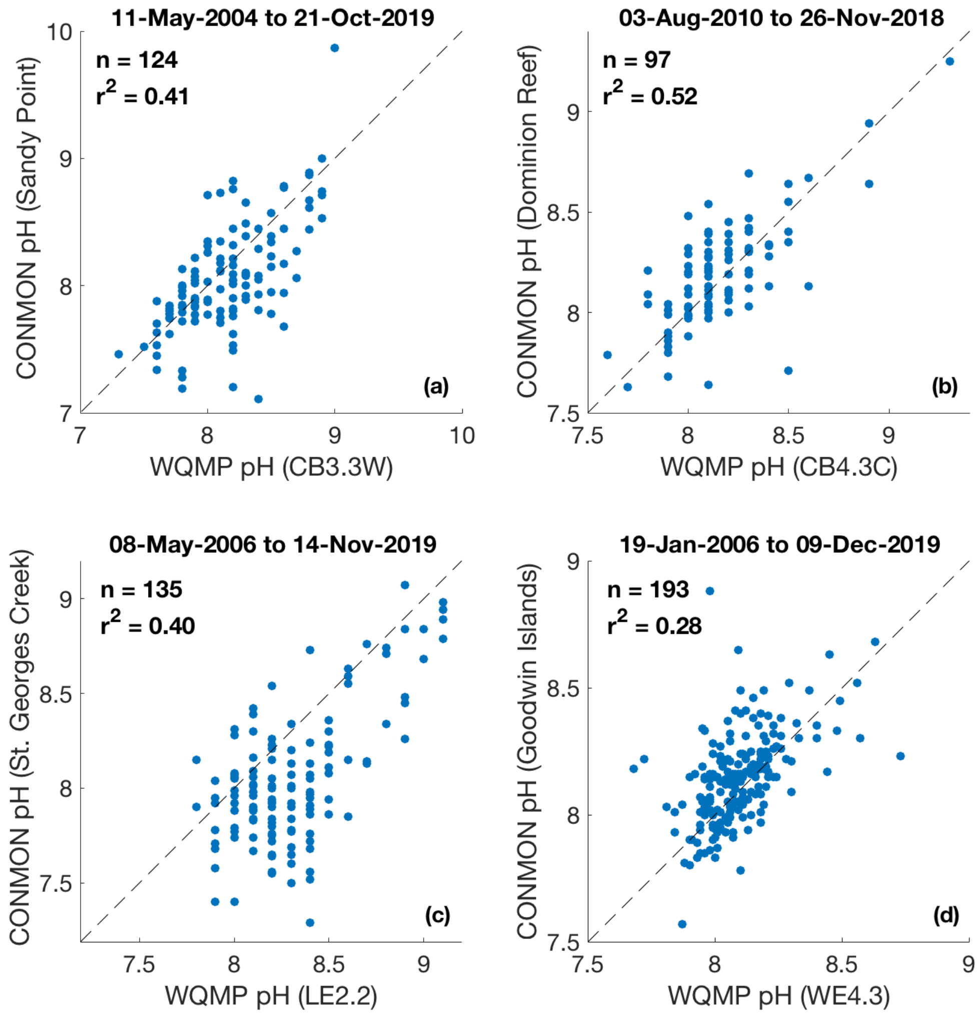

Figure S4. Comparisons of surface pH data collected at CONMON (Continuous Monitoring) stations and adjacent WQMP (Water Quality Monitoring Program) stations. CONMON stations include Sandy Point South Beach, Goose Reef, St. Georges Creek in the Potomac, and Goodwin Islands, and WQMP stations include CB3.3W, CB4.3C, LE2.2 and WE4.3 (Figure 1). In order to compare two datasets at a consistent sampling frequency, high-frequency (15-minute interval) CONMON pH data are resampled at the times when WQMP pH data are available.

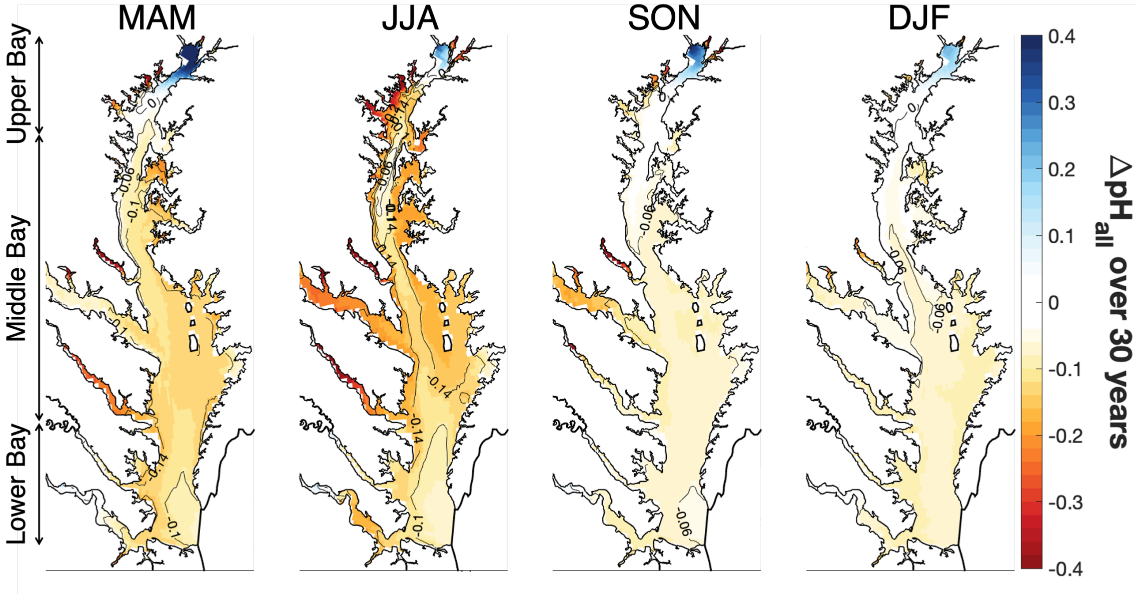

Figure S5. Overall changes in bottom pH due to all global and local stressors combined in four seasons. ΔpH_{all} = *All* – Ref_{1985}. (MAM = spring, JJA = summer, SON = fall, and DJF = winter).

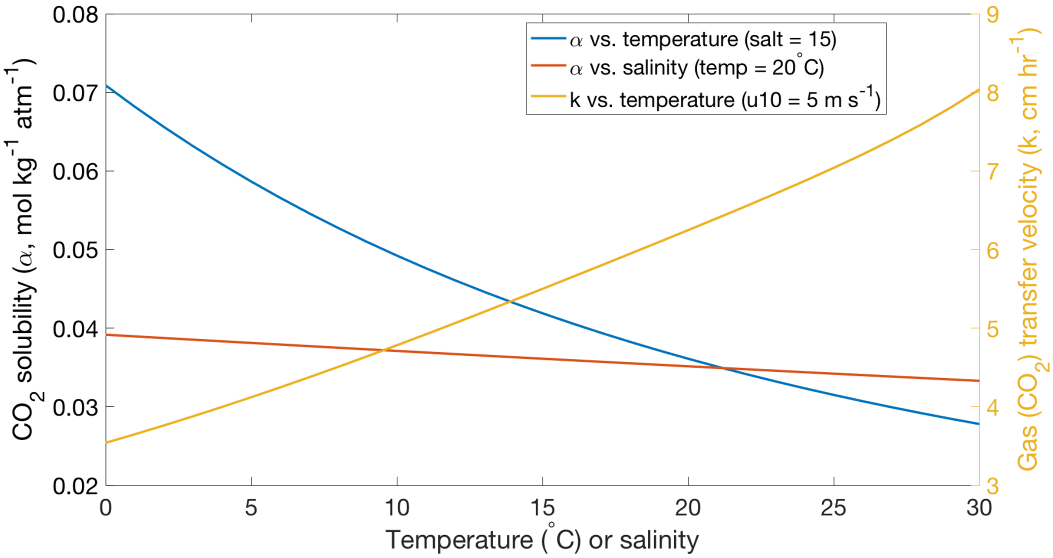

Figure S6. Sensitivity of CO_2 solubility (α) to water temperature (salinity = 15, blue line) and salinity (temperature = 20 °C, red line); sensitivity of gas transfer velocity (k) to water temperature (10 m wind velocity = 5 m s^{-1}). If water temperature increases from 0 °C to 30 °C (approximate temperature range in the Chesapeake Bay), solubility decreases by 61%, and gas transfer velocity increases by 117%.

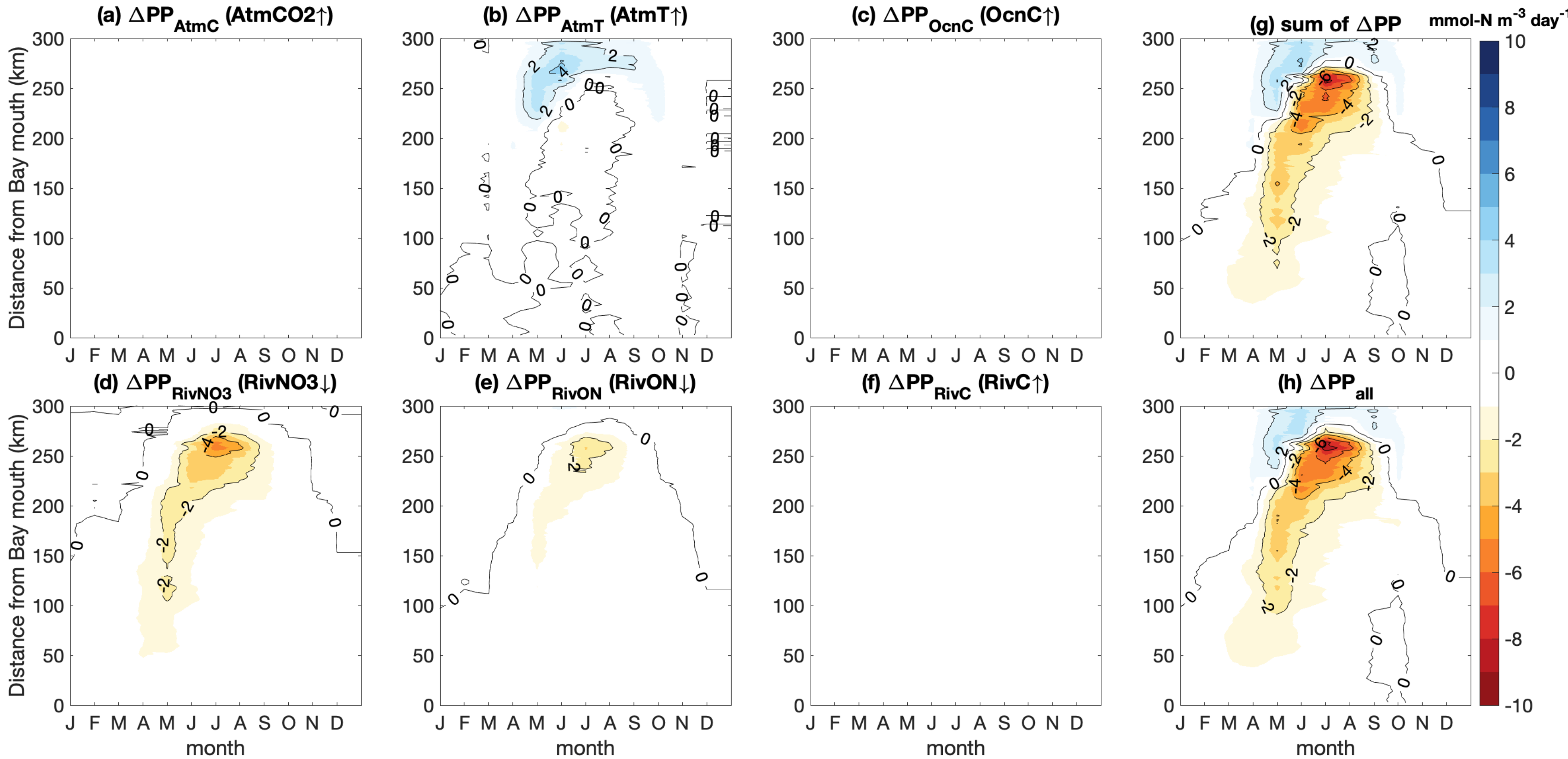

Figure S7. Seasonal cycle of the 30-year changes (Δ) in surface primary production (mmol N m^{-3} day^{-1}) along the main stem due to: (a) increased atmospheric CO_2, (b) increased atmospheric thermal forcing, (c) increased oceanic DIC concentrations, (d) decreased riverine NO_3^- concentrations, (e) decreased riverine organic nitrogen concentrations, (f) increased riverine TA and DIC concentrations, (g) sum of the Δ in (a)-(f), and (h) all six stressors combined. Δ = sensitivity test – Ref_{1985}.

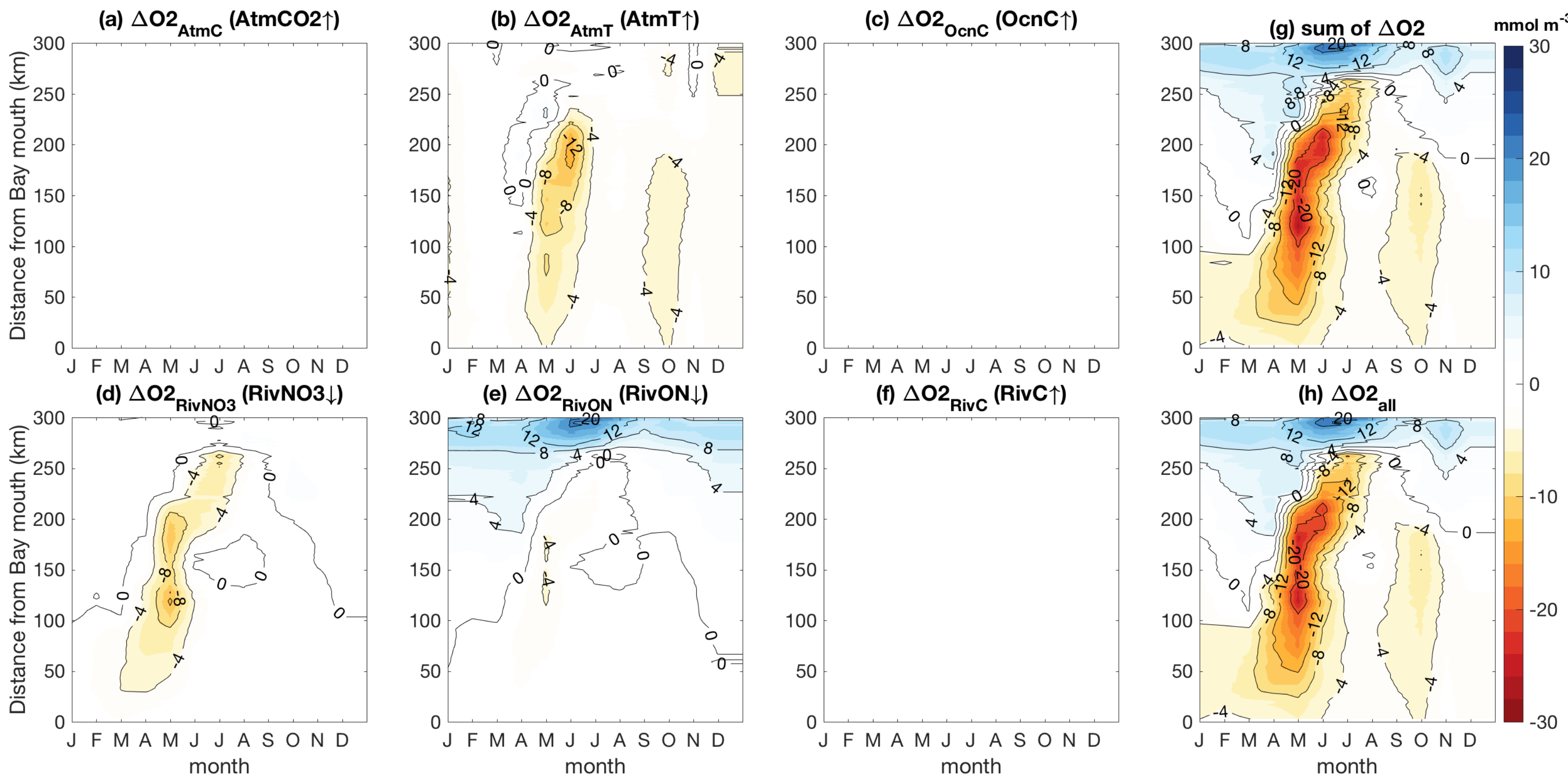

Figure S8. Seasonal cycle of the 30-year changes (Δ) in surface dissolved oxygen (mmol m^{-3}) along the main stem due to: (a) increased atmospheric CO_2, (b) increased atmospheric thermal forcing, (c) increased oceanic DIC concentrations, (d) decreased riverine NO_3^- concentrations, (e) decreased riverine organic nitrogen concentrations, (f) increased riverine TA and DIC concentrations, (g) sum of the Δ in (a)-(f), and (h) all six stressors combined. Δ = sensitivity test – Ref_{1985}.

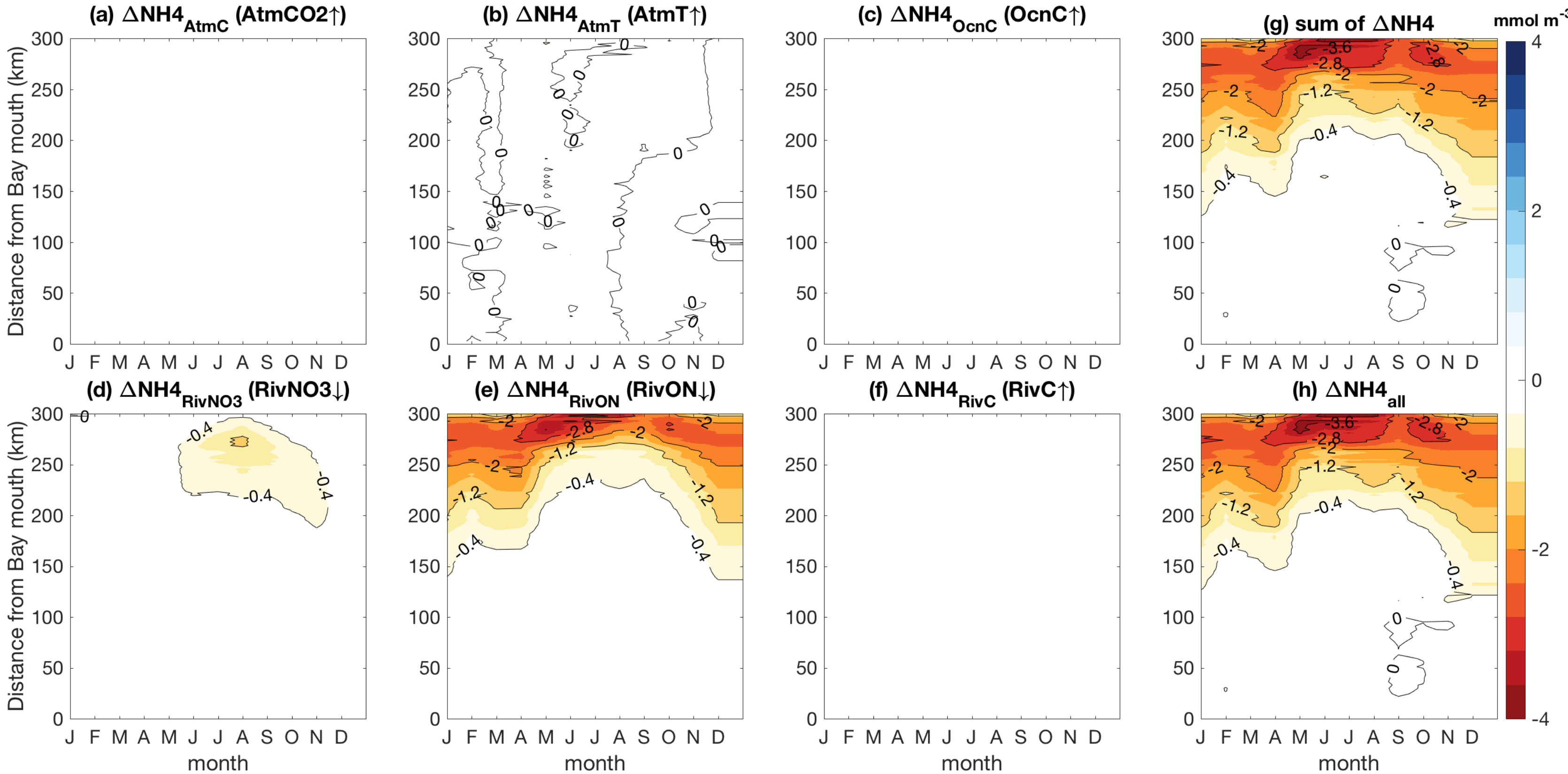

Figure S9. Seasonal cycle of the 30-year changes (Δ) in surface ammonium (mmol m^{-3}) along the main stem due to: (a) increased atmospheric CO_2, (b) increased atmospheric thermal forcing, (c) increased oceanic DIC concentrations, (d) decreased riverine NO_3^- concentrations, (e) decreased riverine organic nitrogen concentrations, (f) increased riverine TA and DIC concentrations, (g) sum of the Δ in (a)-(f), and (h) all six stressors combined. Δ = sensitivity test – *Ref*$_{1985}$.

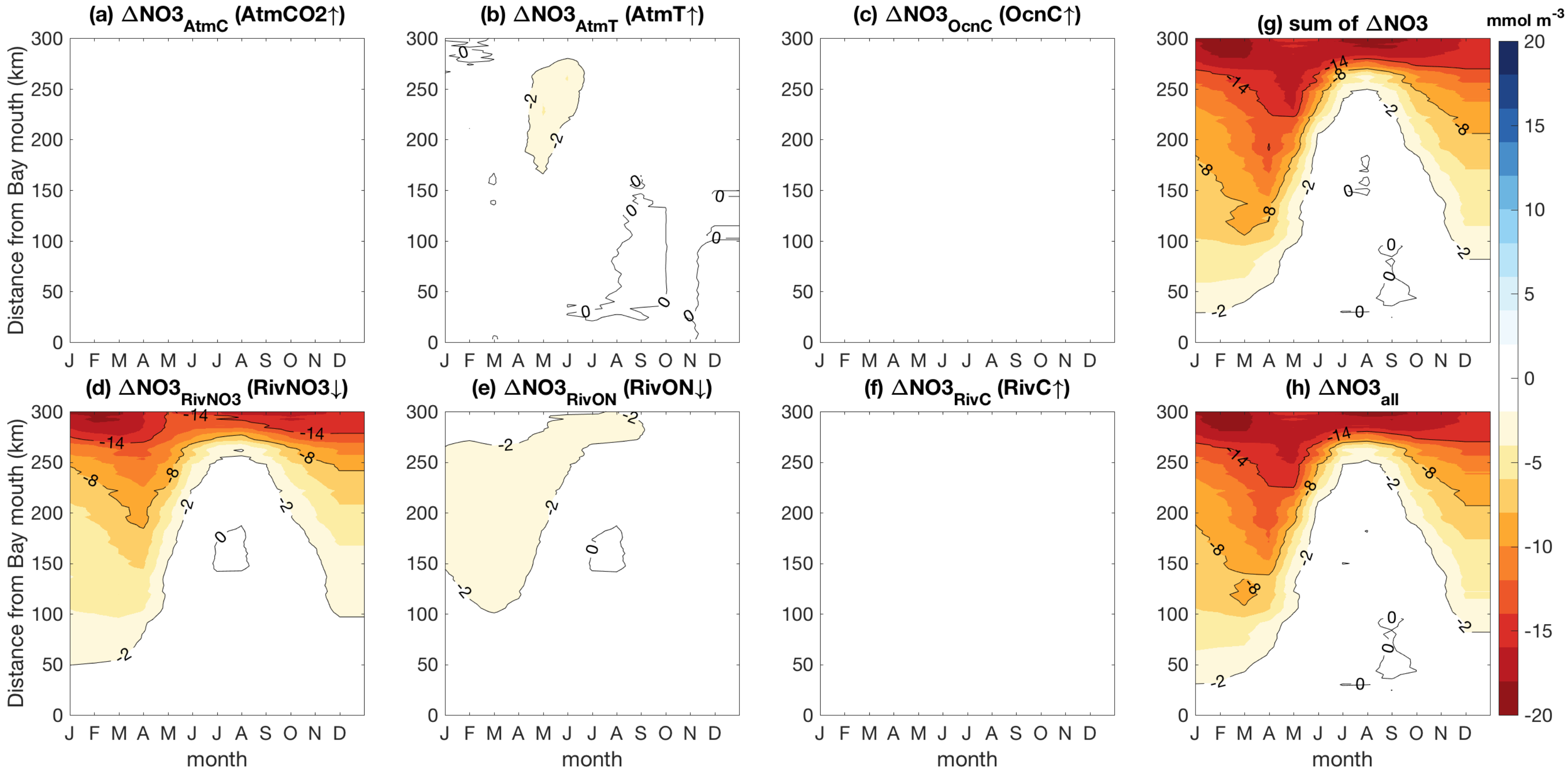

Figure S10. Seasonal cycle of the 30-year changes (Δ) in surface nitrate (mmol m^{-3}) along the main stem due to: (a) increased atmospheric CO_2, (b) increased atmospheric thermal forcing, (c) increased oceanic DIC concentrations, (d) decreased riverine NO_3^- concentrations, (e) decreased riverine organic nitrogen concentrations, (f) increased riverine TA and DIC concentrations, (g) sum of the Δ in (a)-(f), and (h) all six stressors combined. Δ = sensitivity test – Ref_{1985}.

Table S1. Summary of model skill metrics calculated for physical and biogeochemical fields throughout the water column (1985–1989).

Variable	Mean ± standard deviation		Bias	Unbiased RMSD*	RMSD	N&
	Model	*Observation*				
Temperature (°C)	16.99 ± 7.62	16.42 ± 7.91	0.57	–1.25	1.37	18749
Salinity	19.79 ± 4.78	19.05 ± 5.00	0.74	–1.95	2.09	18603
TA# (meq m^{-3})	1478 ± 150	1301 ± 177	177	–242.34	299.64	164
pH (NBS)	7.99 ± 0.38	7.71 ± 0.38	0.28	0.31	0.41	7963
Oxygen (mg L^{-1})	7.63 ± 2.97	7.35 ± 3.23	0.28	–1.47	1.49	18047

*RMSD refers to root-mean squared difference. Unbiased RMSD represents the RMSD after removing the mean from the model estimates or observations (Jolliff et al., 2009).
&N is the total number of data points collected at 18 stations (Fig. 1) from January 1985 to December 1989.
#TA data were only available at CB3.3C (1986–1989) among the examined 18 stations.
All these data were collected by WQMP, and the accuracy of pH measurements is 0.2 pH units. Because of the change in pH measurement protocols at stations to the south of the Potomac River around 1996 (see Hermann et al., 2020 for details), only pH data to the north of the Potomac River were used for model evaluation in this table.

Table S2. Rate of change in surface pH (decade^{-1}) computed at 17 mainstem stations from WQMP data and model simulations.

Station		Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
CB 2.1	Obs[&]	0.15 ±0.09	0.23 ±0.11	0.14 ±0.06	0.02 ±0.09	–0.04 ±0.11	0.18 ±0.12	0.24 ±0.11	0.13 ±0.10	0.08 ±0.07	–0.01 ±0.08	0.25 ±0.06	0.42 ±0.06
	Mod[#]	0.04 ±0.00	0.07 ±0.00	0.11 ±0.00	0.15 ±0.00	0.14 ±0.00	0.06 ±0.00	0.01 ±0.00	0.01 ±0.00	0.05 ±0.00	0.09 ±0.00	0.08 ±0.00	0.05 ±0.00
CB 2.2	Obs	0.25 ±0.06	0.17 ±0.10	0.05 ±0.06	0.03 ±0.05	0.04 ±0.07	0.05 ±0.04	0.03 ±0.03	0.04 ±0.06	–0.02 ±0.06	0.04 ±0.05	0.17 ±0.03	0.31 ±0.08
	Mod	0.02 ±0.00	0.04 ±0.00	0.06 ±0.00	0.08 ±0.00	0.07 ±0.00	0.02 ±0.00	–0.02 ±0.00	–0.03 ±0.00	0.01 ±0.00	0.04 ±0.00	0.05 ±0.00	0.03 ±0.00
CB 3.1	Obs	0.18 ±0.05	0.12 ±0.09	0.10 ±0.07	0.07 ±0.04	0.02 ±0.06	0.07 ±0.05	0.01 ±0.05	0.07 ±0.06	0.04 ±0.07	0.08 ±0.04	0.19 ±0.03	0.26 ±0.05
	Mod	0.01 ±0.00	0.01 ±0.00	0.01 ±0.00	0.02 ±0.00	0.02 ±0.00	–0.02 ±0.00	–0.06 ±0.00	–0.05 ±0.00	–0.02 ±0.00	0.01 ±0.00	0.02 ±0.00	0.01 ±0.00
CB 3.2	Obs	0.09 ±0.11	0.15 ±0.09	0.09 ±0.09	0.02 ±0.06	0.25 ±0.11	–0.04 ±0.07	–0.09 ±0.06	–0.10 ±0.07	–0.11 ±0.08	0.10 ±0.05	0.15 ±0.07	0.21 ±0.06
	Mod	0.01 ±0.00	0.01 ±0.00	0.01 ±0.00	0.02 ±0.00	0.02 ±0.00	–0.03 ±0.00	–0.07 ±0.00	–0.06 ±0.00	–0.03 ±0.00	0.01 ±0.00	0.02 ±0.00	0.00 ±0.00
CB 3.3C	Obs	0.19 ±0.09	–0.06 ±0.08	0.12 ±0.09	0.03 ±0.08	0.02 ±0.12	–0.05 ±0.09	–0.08 ±0.06	–0.13 ±0.08	–0.17 ±0.08	0.08 ±0.06	0.10 ±0.07	0.16 ±0.08
	Mod	0.00 ±0.00	0.00 ±0.00	0.00 ±0.00	0.01 ±0.00	0.01 ±0.00	–0.05 ±0.00	–0.08 ±0.00	–0.06 ±0.00	–0.03 ±0.00	0.00 ±0.00	0.01 ±0.00	0.00 ±0.00
CB 4.1C	Obs	0.14 ±0.08	0.00 ±0.06	0.09 ±0.06	0.14 ±0.08	0.05 ±0.12	–0.08 ±0.07	–0.04 ±0.05	–0.17 ±0.05	–0.20 ±0.06	0.02 ±0.06	0.05 ±0.05	0.11 ±0.07
	Mod	0.00 ±0.00	–0.01 ±0.00	–0.01 ±0.00	–0.01 ±0.00	–0.02 ±0.00	–0.07 ±0.00	–0.08 ±0.00	–0.05 ±0.00	–0.03 ±0.00	–0.01 ±0.00	0.00 ±0.00	0.00 ±0.00
CB 4.2C	Obs	0.11 ±0.07	0.00 ±0.07	0.08 ±0.05	0.07 ±0.07	0.00 ±0.10	–0.10 ±0.05	–0.02 ±0.04	–0.13 ±0.05	–0.09 ±0.05	0.01 ±0.06	0.01 ±0.05	0.08 ±0.07
	Mod	0.00 ±0.00	–0.01 ±0.00	–0.01 ±0.00	–0.01 ±0.00	–0.04 ±0.00	–0.08 ±0.00	–0.08 ±0.00	–0.05 ±0.00	–0.03 ±0.00	–0.02 ±0.00	0.00 ±0.00	–0.01 ±0.00

CB 4.3C	Obs	0.10 ±0.08	0.00 ±0.07	0.08 ±0.05	0.13 ±0.08	0.00 ±0.11	–0.17 ±0.06	–0.01 ±0.04	–0.11 ±0.05	–0.09 ±0.05	0.01 ±0.05	–0.01 ±0.05	0.07 ±0.07
	Mod	0.00 ±0.00	–0.01 ±0.00	–0.01 ±0.00	0.00 ±0.00	–0.04 ±0.00	–0.08 ±0.00	–0.08 ±0.00	–0.05 ±0.00	–0.04 ±0.00	–0.02 ±0.00	0.00 ±0.00	–0.01 ±0.00
CB 4.4	Obs	0.10 ±0.08	0.02 ±0.06	0.09 ±0.05	0.05 ±0.06	–0.02 ±0.10	–0.05 ±0.06	–0.06 ±0.04	–0.11 ±0.05	–0.15 ±0.06	–0.01 ±0.05	0.00 ±0.05	0.09 ±0.07
	Mod	–0.01 ±0.00	–0.01 ±0.00	–0.02 ±0.00	–0.01 ±0.00	–0.06 ±0.00	–0.08 ±0.00	–0.07 ±0.00	–0.04 ±0.00	–0.03 ±0.00	–0.03 ±0.00	–0.01 ±0.00	–0.02 ±0.00
CB 5.2	Obs	0.01 ±0.09	0.10 ±0.07	0.06 ±0.04	–0.02 ±0.06	–0.08 ±0.07	–0.11 ±0.04	–0.10 ±0.03	–0.06 ±0.03	–0.09 ±0.04	0.03 ±0.04	–0.01 ±0.04	0.08 ±0.06
	Mod	–0.01 ±0.00	–0.01 ±0.00	–0.02 ±0.00	–0.03 ±0.00	–0.07 ±0.00	–0.08 ±0.00	–0.07 ±0.00	–0.04 ±0.00	–0.03 ±0.00	–0.03 ±0.00	–0.02 ±0.00	–0.02 ±0.00
CB 5.3	Obs	–0.10 ±0.09	0.09 ±0.08	0.12 ±0.05	–0.01 ±0.05	–0.05 ±0.06	–0.01 ±0.03	–0.09 ±0.04	–0.07 ±0.03	–0.07 ±0.04	0.08 ±0.03	–0.01 ±0.04	0.06 ±0.07
	Mod	–0.02 ±0.00	–0.02 ±0.00	–0.02 ±0.00	–0.03 ±0.00	–0.07 ±0.00	–0.08 ±0.00	–0.06 ±0.00	–0.05 ±0.00	–0.03 ±0.00	–0.03 ±0.00	–0.03 ±0.00	–0.02 ±0.00
CB5. 4	Obs	0.11 ±0.13	0.12 ±0.05	0.06 ±0.07	0.11 ±0.10	–0.19 ±0.06	–0.01 ±0.05	–0.11 ±0.04	0.00 ±0.05	0.04 ±0.04	0.07 ±0.08	0.08 ±0.08	0.26 ±0.13
	Mod	–0.02 ±0.00	–0.02 ±0.00	–0.02 ±0.00	–0.04 ±0.00	–0.06 ±0.00	–0.07 ±0.00	–0.06 ±0.00	–0.04 ±0.00	–0.03 ±0.00	–0.03 ±0.00	–0.03 ±0.00	–0.03 ±0.00
CB 5.5	Obs	0.17 ±0.13	0.07 ±0.08	0.08 ±0.10	–0.01 ±0.07	–0.12 ±0.06	–0.02 ±0.04	–0.13 ±0.04	–0.03 ±0.05	0.01 ±0.05	0.16 ±0.10	0.10 ±0.08	0.06 ±0.06
	Mod	–0.02 ±0.00	–0.03 ±0.00	–0.03 ±0.00	–0.04 ±0.00	–0.06 ±0.00	–0.07 ±0.00	–0.06 ±0.00	–0.04 ±0.00	–0.03 ±0.00	–0.03 ±0.00	–0.03 ±0.00	–0.03 ±0.00
CB 6.1	Obs	0.10 ±0.13	0.07 ±0.08	0.00 ±0.07	–0.02 ±0.11	–0.13 ±0.06	–0.07 ±0.05	–0.14 ±0.03	0.05 ±0.07	–0.03 ±0.04	0.03 ±0.07	0.16 ±0.07	0.04 ±0.05
	Mod	–0.02 ±0.00	–0.03 ±0.00	–0.03 ±0.00	–0.04 ±0.00	–0.07 ±0.00	–0.07 ±0.00	–0.06 ±0.00	–0.04 ±0.00	–0.03 ±0.00	–0.03 ±0.00	–0.03 ±0.00	–0.03 ±0.00
CB 6.2	Obs	0.23 ±0.16	0.08 ±0.07	0.00 ±0.06	–0.13 ±0.06	–0.16 ±0.07	–0.06 ±0.04	–0.13 ±0.03	–0.03 ±0.03	0.01 ±0.03	–0.02 ±0.07	0.11 ±0.11	0.10 ±0.08
	Mod	–0.02 ±0.00	–0.03 ±0.00	–0.03 ±0.00	–0.05 ±0.00	–0.06 ±0.00	–0.07 ±0.00	–0.06 ±0.00	–0.04 ±0.00	–0.03 ±0.00	–0.03 ±0.00	–0.02 ±0.00	–0.03 ±0.00

CB 6.3	Obs	0.02 ±0.07	0.13 ±0.06	0.01 ±0.06	–0.03 ±0.08	–0.11 ±0.07	–0.05 ±0.05	–0.11 ±0.04	–0.02 ±0.04	0.01 ±0.04	0.01 ±0.07	0.10 ±0.06	0.18 ±0.08
	Mod	–0.02 ±0.00	–0.03 ±0.00	–0.04 ±0.00	–0.05 ±0.00	–0.06 ±0.00	–0.06 ±0.00	–0.05 ±0.00	–0.04 ±0.00	–0.03 ±0.00	–0.03 ±0.00	–0.02 ±0.00	–0.03 ±0.00
CB 7.3	Obs	0.05 ±0.11	0.06 ±0.13	0.10 ±0.07	–0.07 ±0.07	–0.04 ±0.11	–0.08 ±0.06	–0.05 ±0.03	–0.02 ±0.02	–0.04 ±0.03	0.12 ±0.10	0.09 ±0.05	0.11 ±0.04
	Mod	–0.02 ±0.00	–0.03 ±0.00	–0.04 ±0.00	–0.04 ±0.00	–0.05 ±0.00	–0.05 ±0.00	–0.04 ±0.00	–0.03 ±0.00	–0.02 ±0.00	–0.02 ±0.00	–0.02 ±0.00	–0.03 ±0.00

[&]Obs represents observed decadal trends (1996–2018); Obs error bars represent standard errors of the linear regression slope.
[#]Mod represents modeled decadal trends which are calculated as ($All - Ref_{1985}$)/3; Mod error bars represent standard errors of the daily estimates of the modeled trend in each month.