

Supporting Information for "Anthropogenic intensification of surface ocean interannual pCO₂ variability"

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Introduction

Text S1.

We construct the full pCO₂ Taylor's expansion decomposition starting with the carbonate chemistry definitions of DIC and TA as in Egleston, Sabine, and Morel (2010):

$$DIC = [CO_2] + \frac{K_1[CO_2]}{[H^+]} + \frac{K_1K_2[CO_2]}{[H^+]^2} \quad (1)$$

$$TA = \frac{K_1[CO_2]}{[H^+]} + 2\frac{K_1K_2[CO_2]}{[H^+]^2} + \frac{B_{tot}K_b}{(K_b + [H^+])} - [H^+] + \frac{K_w}{[H^+]} \quad (2)$$

Where K_1 and K_2 are defined as Millero, Graham, Huang, Bustos-Serrano, and Pierrot (2006), K_w as Millero (1995) and K_b according to Dickson (1990). From Eq. (1) we can obtain $[H^+]$ and from Eq. (2) we get $[CO_2]$ respectively as:

$$[H^+] = \frac{K_1[CO_2] + \sqrt{K_1^2[CO_2]^2 + 4K_1K_2[CO_2](DIC - [CO_2])}}{2(DIC - [CO_2])} \quad (3)$$

$$[CO_2] = \frac{[H^+]^2}{K_1[H^+] + 2K_1K_2} \left(TA - \frac{B_{tot}K_b}{(K_b + [H^+])} + [H^+] - \frac{K_w}{[H^+]} \right) \quad (4)$$

For $[H^+]$ the positive solution was chosen; the negative root gives a result far from real values. From Eq. (3) and Eq. (4) we can make a Taylor's expansion of $[H^+]$ and $[CO_2]$ respectively as:

$$\begin{aligned} \delta[H^+] &= \frac{\partial[H^+]}{\partial DIC} \Big|_{\overline{CO_2}, \overline{DIC}} \delta DIC + \frac{\partial[H^+]}{\partial [CO_2]} \Big|_{\overline{CO_2}, \overline{DIC}} \delta [CO_2] + \frac{\partial[H^+]}{\partial T} \Big|_{\overline{CO_2}, \overline{DIC}} \delta T + \frac{\partial[H^+]}{\partial S} \Big|_{\overline{CO_2}, \overline{DIC}} \delta S \\ \delta[CO_2] &= \frac{\partial[CO_2]}{\partial TA} \Big|_{\overline{TA}, \overline{H}} \delta TA + \frac{\partial[CO_2]}{\partial [H^+]} \Big|_{\overline{TA}, \overline{H}} \delta [H^+] + \frac{\partial[CO_2]}{\partial T} \Big|_{\overline{TA}, \overline{H}} \delta T + \frac{\partial[CO_2]}{\partial S} \Big|_{\overline{TA}, \overline{H}} \delta S \end{aligned} \quad (5)$$

The overbars indicate the climatologies of the variables in which the derivatives are evaluated. Finally, we insert $\delta[H^+]$ from Eq. (5) into Eq. (6), to get $[CO_2]$ in terms of DIC, TA, T and S:

$$\begin{aligned} \delta[CO_2] &= \left[1 - \frac{\partial[CO_2]}{\partial [H^+]} \Big|_{\overline{TA}, \overline{H}} \frac{\partial[H^+]}{\partial [CO_2]} \Big|_{\overline{CO_2}, \overline{DIC}} \right]^{-1} \cdot \left[\frac{\partial[CO_2]}{\partial TA} \Big|_{\overline{TA}, \overline{H}} \delta TA \right. \\ &\quad \left. + \frac{\partial[CO_2]}{\partial [H^+]} \Big|_{\overline{TA}, \overline{H}} \frac{\partial[H^+]}{\partial DIC} \Big|_{\overline{CO_2}, \overline{DIC}} \delta DIC \right. \\ &\quad \left. + \left(\frac{\partial[CO_2]}{\partial T} \Big|_{\overline{TA}, \overline{H}} + \frac{\partial[CO_2]}{\partial [H^+]} \Big|_{\overline{TA}, \overline{H}} \frac{\partial[H^+]}{\partial T} \Big|_{\overline{CO_2}, \overline{DIC}} \right) \delta T \right] \end{aligned}$$

$$+\left(\frac{\partial[CO_2]}{\partial S}\bigg|_{\overline{T},\overline{S}}+\frac{\partial[CO_2]}{\partial[H^+]}\bigg|_{\overline{T},\overline{S}}\frac{\partial[H^+]}{\partial S}\bigg|_{\overline{CO_2},\overline{DIC}}\right)\delta S\Big] \quad (7)$$

Comparing the terms from Eq.(7) to the desired Taylor's expansion:

$$\delta pCO_2 \approx \frac{\partial pCO_2}{\partial DIC}\bigg|_{\overline{T},\overline{S}}\delta DIC + \frac{\partial pCO_2}{\partial TA}\bigg|_{\overline{T},\overline{S}}\delta TA + \frac{\partial pCO_2}{\partial T}\bigg|_{\overline{T},\overline{S}}\delta T + \frac{\partial pCO_2}{\partial S}\bigg|_{\overline{T},\overline{S}}\delta S \quad (8)$$

We can identify the derivatives from Eq.(8), as follows:

$$\begin{aligned}
 \left. \frac{\partial pCO_2}{\partial TA} \right|_{\frac{\overline{TA}, \overline{DIC}}{\overline{T}, \overline{S}}} &= \overline{pCO_2} \cdot \frac{-\overline{TA}_c}{\overline{DIC} \cdot \Theta - \overline{TA}_c^2} \\
 \left. \frac{\partial pCO_2}{\partial DIC} \right|_{\frac{\overline{TA}, \overline{DIC}}{\overline{T}, \overline{S}}} &= \overline{pCO_2} \cdot \frac{\Theta}{\overline{DIC} \cdot \Theta - \overline{TA}_c^2} \\
 \left. \frac{\partial pCO_2}{\partial T} \right|_{\frac{\overline{TA}, \overline{DIC}}{\overline{T}, \overline{S}}} &= \overline{pCO_2} \cdot \frac{1}{\overline{DIC} \cdot \Theta - \overline{TA}_c^2} \left[\overline{TA}_c \cdot \left(\frac{\partial Alk_c}{\partial T} + \frac{\partial [B(OH)_4^-]}{\partial T} + \frac{\partial [OH^-]}{\partial T} \right) - \Theta \cdot \frac{\partial (DIC - [CO_2])}{\partial T} \right] - \frac{\overline{pCO_2}}{\overline{K_0}(T, S)} \frac{\partial K_0(T, S)}{\partial T} \\
 \left. \frac{\partial pCO_2}{\partial S} \right|_{\frac{\overline{TA}, \overline{DIC}}{\overline{T}, \overline{S}}} &= \overline{pCO_2} \cdot \frac{1}{\overline{DIC} \cdot \Theta - \overline{TA}_c^2} \left[\overline{TA}_c \cdot \left(\frac{\partial \overline{TA}_c}{\partial S} + \frac{\partial [B(OH)_4^-]}{\partial S} + \frac{\partial [OH^-]}{\partial S} \right) - \Theta \cdot \frac{\partial (DIC - [CO_2])}{\partial S} \right] - \frac{\overline{pCO_2}}{\overline{K_0}(T, S)} \frac{\partial K_0(T, S)}{\partial S}
 \end{aligned} \tag{9}$$

where $\Theta = [HCO_3^-] + 4[CO_3^{2-}] + \frac{[B(OH)_4^-][H^+]}{(k_b + [H^+])} + [H^+] + [OH^-]$ and $\overline{Alk}_c = [HCO_3^-] + 2[CO_3^{2-}]$.

Below are some details of the specific concentrations derivatives.

$$\begin{aligned}
 \frac{\partial Alk_c}{\partial T, S} &= \frac{[CO_2]}{[H^+]^2} \left(\frac{\partial k_1}{\partial T, S} [H^+] + 2k_1 \frac{\partial k_2}{\partial T, S} + 2k_2 \frac{\partial k_1}{\partial T, S} \right) \\
 \frac{\partial (DIC - [CO_2])}{\partial T, S} &= \frac{[CO_2]}{[H^+]^2} \left(\frac{\partial k_1}{\partial T, S} [H^+] + k_1 \frac{\partial k_2}{\partial T, S} + k_2 \frac{\partial k_1}{\partial T, S} \right) \\
 \frac{\partial [B(OH)_4^-]}{\partial T} &= \frac{B_{tot}[H^+]}{(k_b + [H^+])^2} \frac{\partial k_b}{\partial T} \\
 \frac{\partial [B(OH)_4^-]}{\partial S} &= \frac{B_{tot}[H^+]}{(k_b + [H^+])^2} \frac{\partial k_b}{\partial S} + \frac{k_b}{(k_b + [H^+])} \frac{\partial B_{tot}}{\partial S} \\
 \frac{\partial [OH^-]}{\partial T, S} &= \frac{1}{[H^+]} \frac{\partial k_w}{\partial T, S}
 \end{aligned} \tag{10}$$

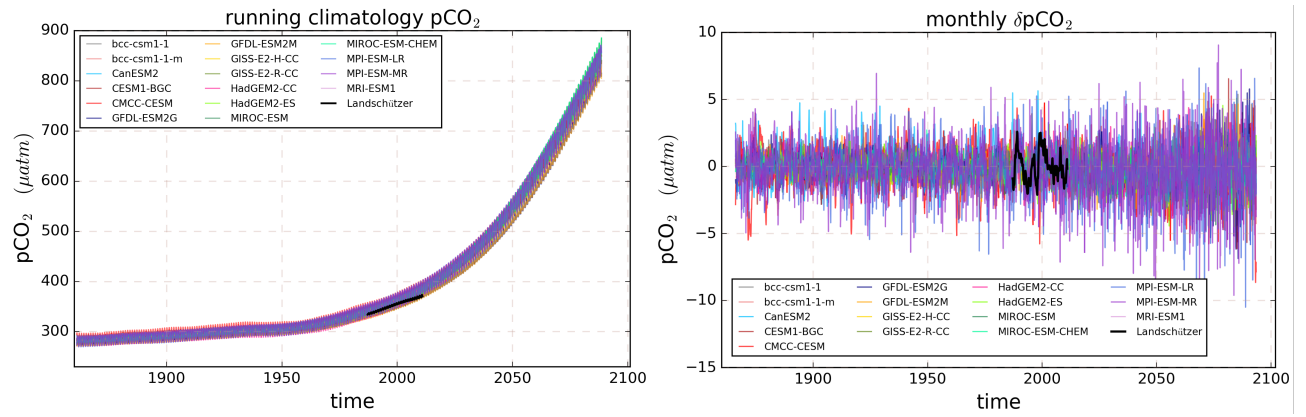


Figure S1. Time series (1866-2095) of pCO₂ as a) 11 years running climatology and b) monthly anomaly (calculated as the deviation from the climatology), for 13 different CIMP5 models, under RCP8.5 scenario. Overlaid in black is the anomalies from the observation-based estimations of Landschützer et al. (2017)

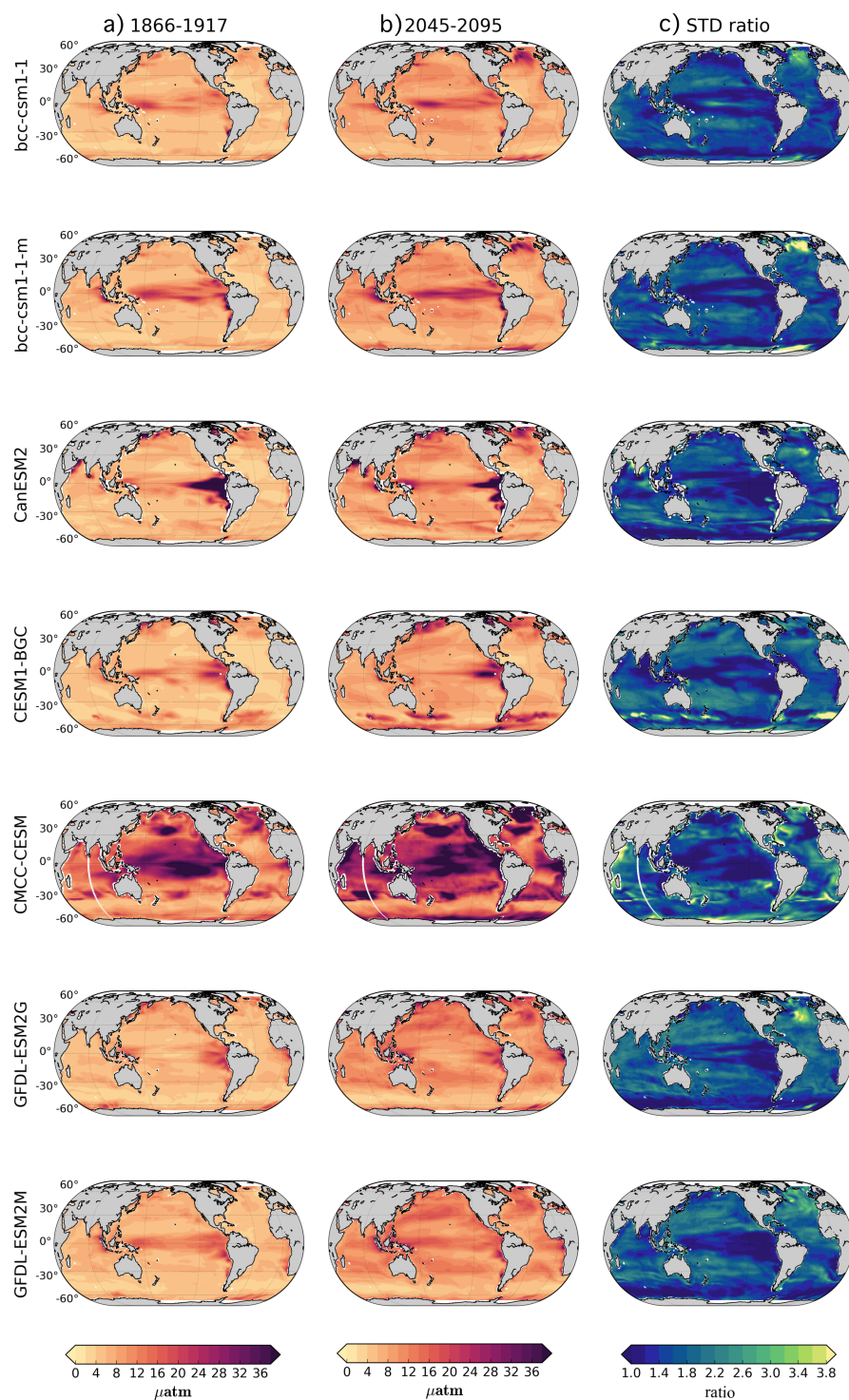


Figure S2. pCO₂'s interannual anomalies, shown as a) 1866-1916 and b) 2045-2095 standard deviations. c) shows the 2045-2095 STD divided by 1866-1916 STD. Each row shows a different CMIP5 model.

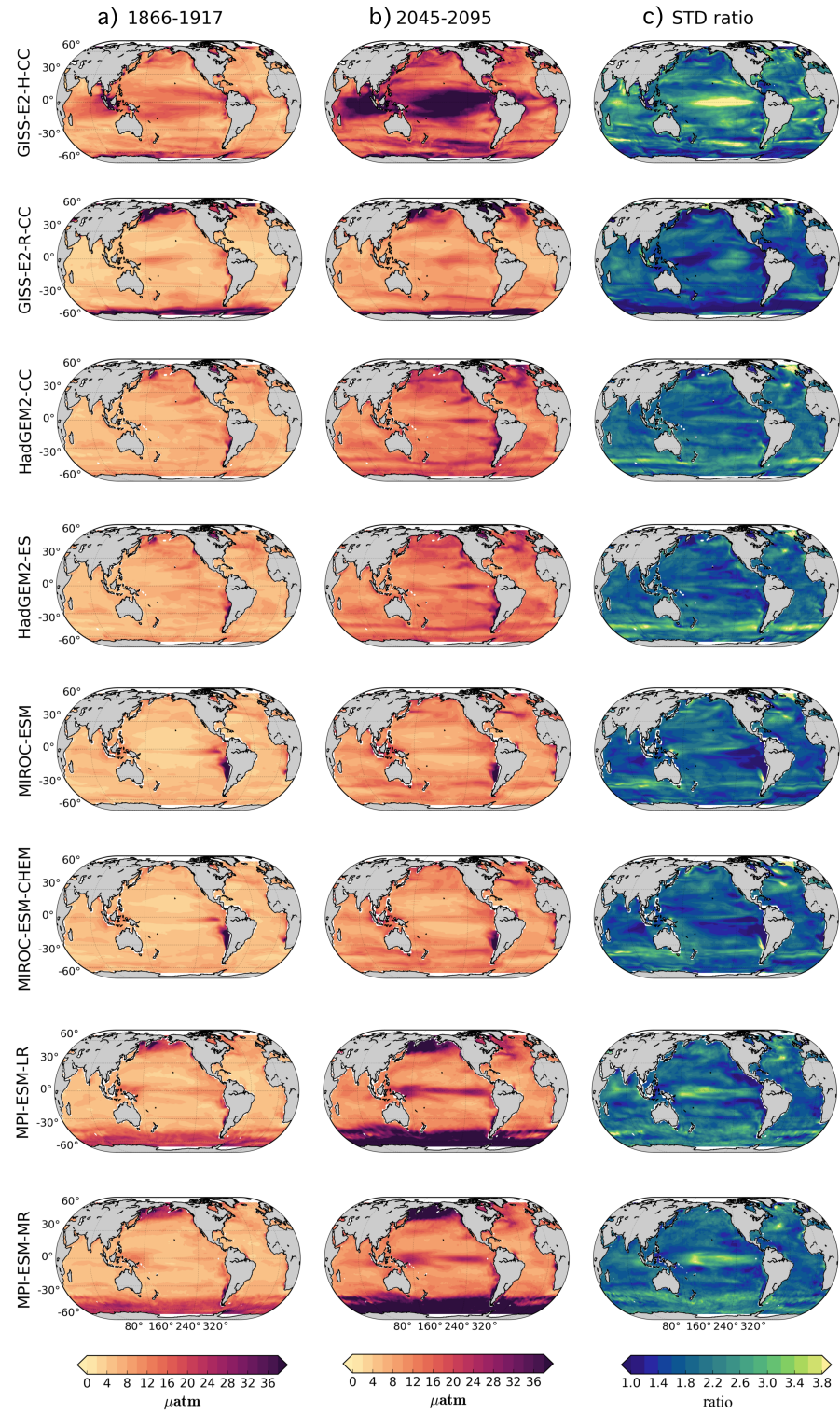


Figure S3. Same as Figure S2 but for different models.

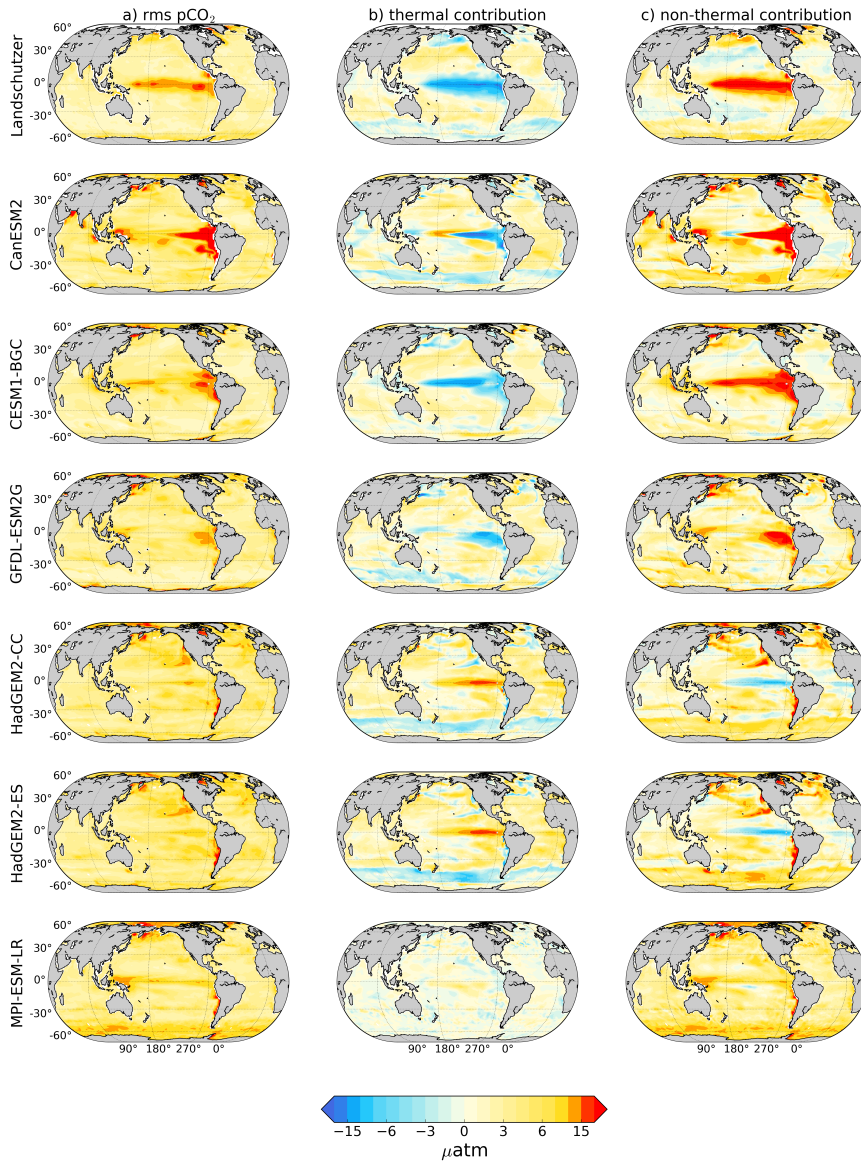


Figure S4. 1987-2010 values of root mean square (RMS) for a) $p\text{CO}_2$ anomalies and the b) thermal and c) non-thermal contributions to $p\text{CO}_2$'s RMS. The contributions are defined as the regression coefficients between the components (either thermal or non-thermal) and the $p\text{CO}_2$ anomaly, following the method of Doney et al. (2009). The thermal and non-thermal components are calculated as Takahashi et al. (2002). The first row shows the observation-based results of Landschützer et al. (2017). The anomalies were calculated with the method of Landschützer et al. (2018), to compare with their results. The data was first filtered with a 12 month mean, and then detrended with a quadratic polynomial.

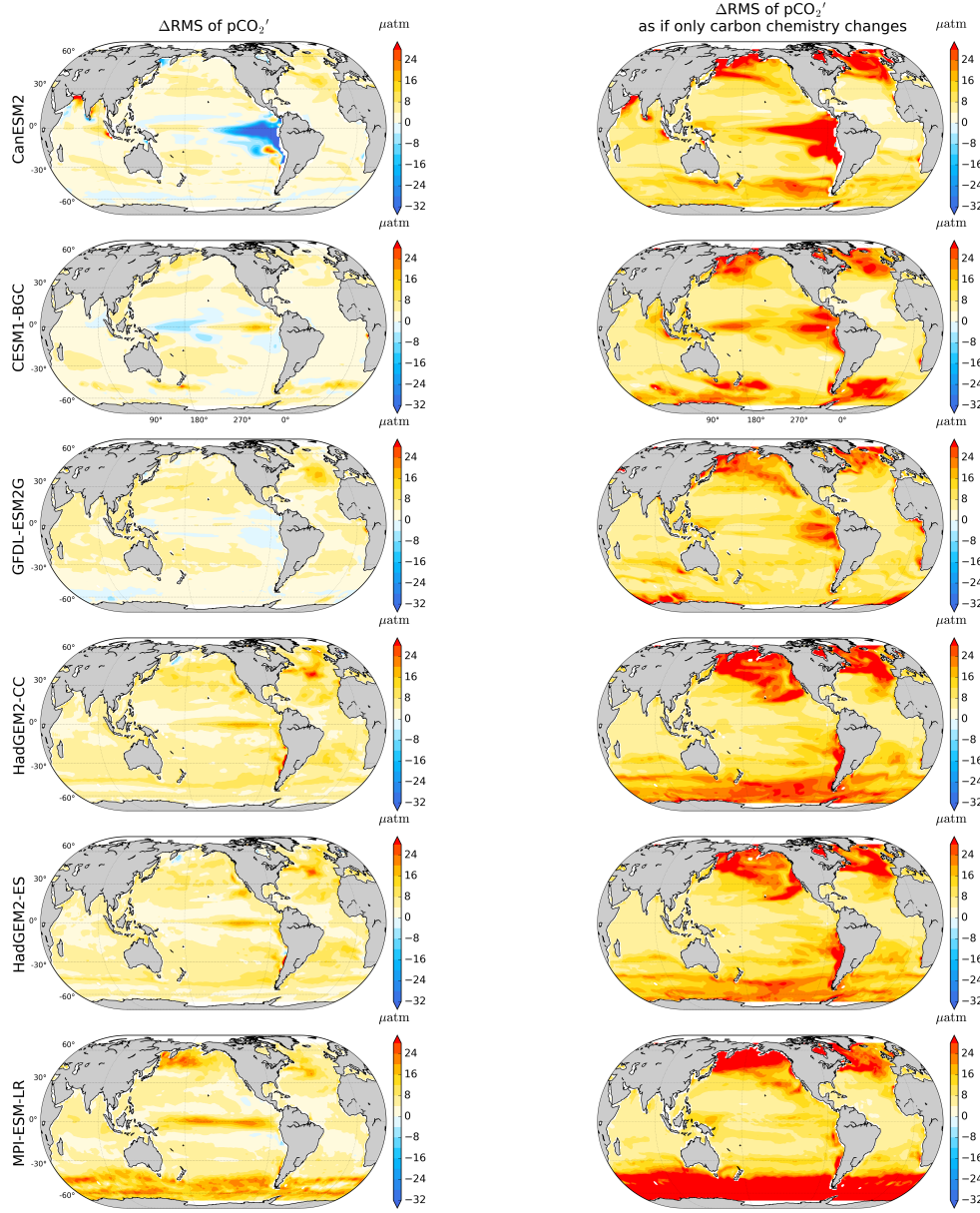


Figure S5. Causes of increasing pCO₂' variability: Total change (measured as 2045-2095 minus 1870-1920 values) of **a)** the RMS of pCO₂' and **b)** RMS of pCO₂' when only the value of $\overline{\text{pCO}_2}$, γ_{DIC_s} and γ_T vary, but we keep constant the 1870-1920 value of the DIC_s' and T' interannual anomalies. Each row represents a different model.

References

Dickson, A. G. (1990). Thermodynamics of the dissociation of boric acid in synthetic seawater

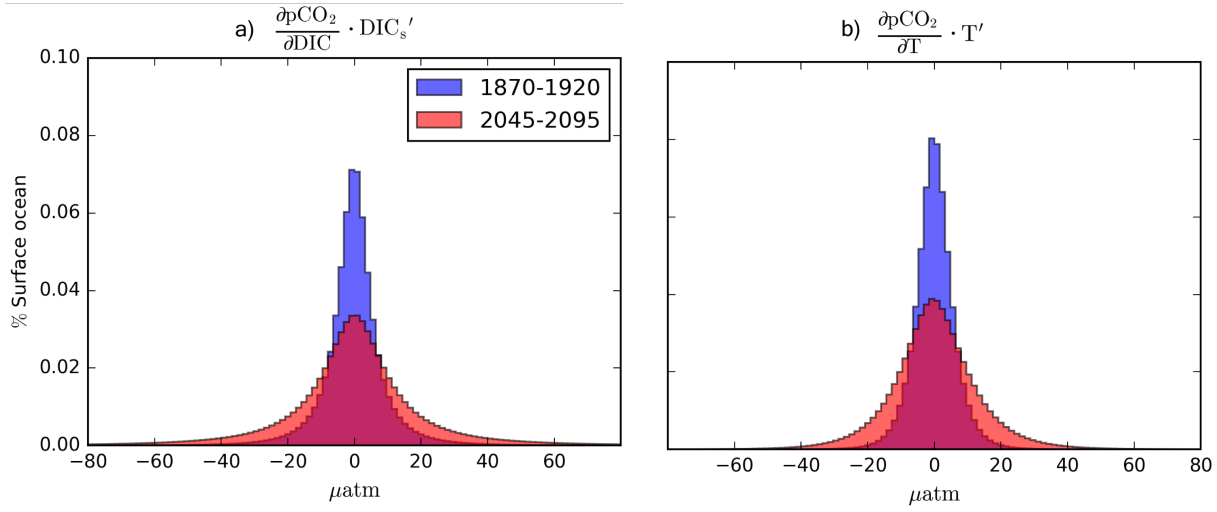


Figure S6. Increase on DIC_s and T contributions to pCO₂ interannual variability.

a) and **b)** show the distributions of the DIC_s and T terms that control the pCO₂ anomalies, as calculated in Eq. (1) of the main text. The distributions show 600 monthly values for the 1870-1920 (blue) and 2045-2095 (red) periods for every point of the ocean between 180°E to 180°W and 60°S to 60°N.

- from 273.15 to 318.15 K. *Deep-Sea Research Part A. Oceanographic Research Papers*, 37, 755–766.
- Doney, S. C., Lima, I., Feely, R. A., Glover, D. M., Lindsay, K., Mahowald, N., . . . Wanninkhof, R. (2009). Mechanisms governing interannual variability in upper-ocean inorganic carbon system and air–sea CO₂ fluxes: Physical climate and atmospheric dust. *Deep Sea Research Part II: Topical Studies in Oceanography*, 56(8), 640 - 655. doi: <https://doi.org/10.1016/j.dsr2.2008.12.006>
- Egleston, E. S., Sabine, C. L., & Morel, F. M. M. (2010). Revelle revisited: Buffer factors that quantify the response of ocean chemistry to changes in DIC and alkalinity. *Global Biogeochem. Cycles*, 24, GB1002.
- Landschützer, P., Gruber, N., & Bakker, D. (2017). *An updated observation-based global monthly gridded sea surface pCO₂ and air-sea CO₂ flux product from 1982 through 2015 and its monthly climatology (NCEI Accession 0160558). Version 2.2. NOAA National Centers for Environmental Information. Dataset. doi:10.7289/v5z899n6.*
- Landschützer, P., Gruber, N., Bakker, D. C. E., Stemmler, I., & Six, K. D. (2018). Strengthening seasonal marine CO₂ variations due to increasing atmospheric CO₂. *Nat. Clim. Change*, 8, 146–150.
- Millero, F. J. (1995). Thermodynamics of the carbon dioxide system in the oceans. *Geochemica et Cosmochemica Acta*, 59, 661–677.
- Millero, F. J., Graham, T. B., Huang, F., Bustos-Serrano, H., & Pierrot, D. (2006). Dissociation constants of carbonic acid in seawater as a function of salinity and temperature. *Marine Chemistry*, 100(1–2), 80–94.
- Takahashi, T., Sutherland, S. C., Sweeney, C., Poisson, A., Metzl, N., Tilbrook, B., . . . Nojiri,

Y. (2002). Global sea-air CO₂ flux based on climatological surface ocean pCO₂, and seasonal biological and temperature effects. *Deep-Sea Research II*, 49, 1601–1623.