

1 **Increasing river alkalinity slows ocean acidification in the northern Gulf of Mexico**

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10 **Key Points:**

- 11 • We simulated the spatiotemporal variability of ocean acidification progression over the
12 Gulf of Mexico during 1981-2014.
- 13 • Model results showed positive trends in the surface ocean alkalinity, salinity, and
14 temperature influencing acidification trends.
- 15 • Increasing Mississippi river alkalinity substantially lessened the ocean acidification
16 progression on the northern Gulf of Mexico shelf.

17 Abstract

18 Ocean acidification (OA) progression is affected by multiple factors, such as ocean warming,
19 biological production, and runoff. Here we used an ocean-biogeochemical model to assess the
20 impact of river runoff and climate variability on the spatiotemporal patterns of OA in the Gulf of
21 Mexico (GoM) during 1981-2014. The model showed the expected pH and aragonite saturation
22 state (Ω_{Ar}) decline, due to the increase in anthropogenic carbon, with trends close to values
23 reported for the Subtropical North Atlantic. However, significant departures from the basin-
24 averaged pattern were obtained in part of the northern GoM shelf, where pH and Ω_{Ar} increased.
25 Model sensitivity analyses showed that OA progression was counteracted by enhanced alkalinity
26 from the Mississippi-Atchafalaya River System. Our findings highlight that river alkalinity is a
27 key driver of carbon system variability in river-dominated ocean margins and emphasize the need
28 to quantify riverine chemistry to properly assess acidification in coastal waters.

29 Plain Language Summary

30 Although ocean acidification (OA) is mainly driven by the ocean uptake of anthropogenic carbon
31 dioxide from the atmosphere, multiple factors influence its temporal progression, including
32 changes in ocean temperature, biological processes, and river discharge. Here we used numerical
33 model outputs to describe historical OA trends across the Gulf of Mexico (GoM) and identify the
34 main drivers of its spatial variability. We showed that changes in river runoff slowed OA over the
35 northern GoM coast. This was mainly due to an increasing Mississippi river alkalinity
36 concentration, a property related to the water capacity to neutralize acidification. Our results show
37 the importance of alkalinity changes to quantify OA progression in the GoM.

38 1 Introduction

39 Ocean acidification (OA), induced by the ocean uptake of atmospheric anthropogenic CO₂,
40 is affecting global ocean carbon chemistry, leading to a sustained decline in pH, along with an
41 increase in dissolved inorganic carbon (DIC), partial pressure of CO₂ (pCO₂), and calcium
42 carbonate solubility, the latter usually tracked as a decline in aragonite saturation state (Ω_{Ar})
43 (Doney et al., 2009; Gruber et al., 2019). These changes in carbon chemistry are negatively
44 impacting marine species and ecosystems. The most obvious impacts are associated with decreased
45 calcification rates in calcifying organisms, such as corals and shellfish, which results in reduced
46 individual growth and survival (e.g., Hoegh-Guldberg et al., 2007; Waldbusser et al., 2015). OA

47 is a major environmental stressor, which is expected to produce significant changes in marine
48 community structure and the availability of marine resources (Ekstrom et al., 2015; Cross et al.,
49 2019; Doney et al., 2020).

50 Datasets with records extending two or more decades have revealed long-term pCO₂
51 increases consistent with the increase in atmospheric CO₂, but variability is evident across regions
52 (Bates et al., 2014; Lauvset et al., 2015). Major departures from the anthropogenic CO₂-driven
53 changes can be expected in coastal regions, where variability in biological production, coastal
54 currents, temperature, and salinity are more likely to impact carbon chemistry trends (Cai et al.,
55 2011; Turi et al., 2016; Laruelle et al., 2018; Salisbury & Jönsson, 2018). This is particularly true
56 in river dominated ocean margins where the chemistry of river discharge directly influences the
57 ability of coastal waters to counteract acidification (Duarte et al., 2013.). Therefore, sustained
58 observational programs and modeling are required to identify OA progression and causes at
59 regional levels, so that ecosystem and socioeconomic vulnerabilities to OA can be assessed.

60 The Gulf of Mexico (GoM) hosts large spatiotemporal variability in its physical and
61 biogeochemical patterns and is significantly influenced by the Loop Current and the Mississippi-
62 Atchafalaya River System (MARS). The Loop Current transports warm and oligotrophic waters
63 from the Caribbean Sea, and largely defines water properties in the open GoM (Muller-Karger et
64 al., 2015; Damien et al., 2018). The MARS delivers large freshwater and nutrients fluxes to the
65 northern GoM shelf, strongly modulating regional salinity and biochemistry patterns (Dagg &
66 Breed, 2003; Rabalais et al., 2007). A series of observational studies have documented the
67 dominant spatial patterns and seasonal variability of pCO₂ and other carbon system variables in
68 the GoM (e.g., Lohrenz et al., 2018; Wang et al., 2013; Wanninkhof et al., 2015; Hu et al., 2015,
69 2018). However, interannual to multi-decadal variability remains poorly examined due to the lack
70 of sufficiently long time-series capable of discriminating OA trends from natural variability.

71 High-resolution ocean-biogeochemical models can assist in filling observational gaps by
72 describing and attributing ocean chemistry variability over time. Therefore, they are particularly
73 valuable tools for assessing the historical progression of OA and other low-frequency processes
74 that impact the carbon cycle. In a recent study, Gomez et al. (2020) configured and validated an
75 ocean-biogeochemical model for the GoM, examining dominant seasonal patterns in pCO₂ and
76 Ω_{Ar}. For the present study, we used the same model to investigate OA progression. We derived

77 long-term trends for OA indicators during 1981-2014 and performed sensitivity analyses to
78 examine the influence of river runoff and climate variability on OA progression.

79 **2 Methods**

80 We used the ocean-biogeochemical model described and validated in Gomez et al. (2018,
81 2020), which contains 16 state variables, including two inorganic carbon system variables: total
82 alkalinity (TA) and DIC. The ocean-biogeochemical model was implemented in the Regional
83 Ocean Model System (ROMS, Shchepetkin et al., 2005), with a horizontal resolution of ~8 km
84 and 37 sigma-coordinate vertical levels. A third order upstream scheme and a fourth order Akima
85 scheme were used for horizontal and vertical momentum, respectively. A multidimensional
86 positive definite advection transport algorithm (MPDATA) was used for tracer advection, while a
87 Mellor and Yamada 2.5-level closure scheme was used to resolve vertical turbulence. The initial
88 and open boundary conditions were derived from a 25 km horizontal resolution model for the
89 North Atlantic (Liu et al., 2015). Surface fluxes of momentum (6-hour resolution), heat (daily),
90 and precipitation (monthly) were derived from the European Centre for Medium Range Weather
91 Forecasts reanalysis product ERA-Interim (Dee et al., 2011) using a bulk flux parameterization.
92 River discharge, nutrients, TA, and DIC data were obtained from the U.S. Geological Survey for
93 rivers in the U.S. and derived from scientific literature for Mexican rivers (He et al. 2011; Muñoz-
94 Salinas & Castillo, 2015; Martínez-López & Zavala-Hidalgo, 2009). We prescribed a time-
95 evolving monthly series of freshwater discharge for 28 river sources in the U.S., and a
96 climatological discharge for 10 rivers in the U.S. and 11 rivers in Mexico. Due to the lack of
97 continuous long-term records, the time evolving concentration of nutrients, TA, and DIC were
98 prescribed for only the Mississippi and Atchafalaya rivers, while long-term climatological values
99 were prescribed for the other river sources. The partial pressure of atmospheric CO₂ (pCO_{2air}) was
100 prescribed as a continuous nonlinear function (using a third-degree polynomial expression plus
101 four harmonics) adjusted to the monthly pCO_{2air} series from the Mauna Loa Observatory.

102 In addition to the model hindcast, we also conduct two experiments to evaluate the OA
103 progression sensitivity to river runoff changes: the climatological MARS chemistry experiment
104 (CLM_MC) and the climatological rivers experiment (CLM_RIV). In CLM_MC, we used
105 monthly climatological values for the MARS's chemistry (nutrients, DIC, and TA). In CLM_RIV,

we used climatological river discharge values for all rivers, as well as the climatological chemistry for the MARS. The influence of MARS's time evolving chemistry on OA was obtained from the difference between the CLM_MC and hindcast trends, and the added impact of time evolving river discharges and time-evolving MARS chemistry from the difference between the CLM_RIV and hindcast trends. Hence, the difference between the CLM_MC and CLM_RIV trends provided an estimate of the discharge variability impacts on OA. Finally, to evaluate the influence of climate variability on the OA patterns, we conducted the climatological forcing experiment (CLM_FORC), where we prescribed climatological patterns for rivers, surface fluxes and the open boundary conditions at the southern and eastern edges of the model domain. The only exceptions were pCO_{2air} and the open boundary conditions for DIC, which varied as in the model hindcast (following Turi et al., 2016). The climate-variability impact was derived from the difference between the CLM_FORC and hindcast trends.

Monthly outputs of surface DIC (*s*DIC), surface TA (*s*TA), sea surface salinity (SSS), and sea surface temperature (SST) were used to derive simulated in situ patterns of three OA indicators: pCO₂, pH, and Ω_{Ar}. To this effect, we used the CO2SYS program for CO₂ System Calculations (van Heuven et al., 2011). A simple linear regression was used to calculate the trends from the model's monthly anomalies for each variable of interest. Monthly outputs with the monthly climatological mean of 1981-2014 removed (deseasonalized) were referred to as anomalies.

We used a first order Taylor series to decompose the surface pCO₂, pH, and Ω_{Ar} variability into their four driver's components:

$$\Delta\varphi \approx \frac{\partial\varphi}{\partial sDIC} \cdot \Delta sDIC + \frac{\partial\varphi}{\partial sTA} \cdot \Delta sTA + \frac{\partial\varphi}{\partial SSS} \cdot \Delta SSS + \frac{\partial\varphi}{\partial SST} \cdot \Delta SST \quad (1)$$

where Δφ represents the time change for the parameter of interest (either pCO₂, pH, or Ω_{Ar}), and the four right side terms represent the *s*DIC, *s*TA, SSS, and SST contribution to the φ change, respectively. The partial derivatives of the contribution terms were estimated by adding a small perturbation to each driver while keeping the other three terms as constant, using the CO2SYS program for the carbon system calculations.

3 Results

133 The simulated patterns of surface pCO₂, pH, and Ω_{Ar} anomalies produced basin-averaged
134 trends of $1.57 \pm 0.03 \text{ } \mu\text{atm yr}^{-1}$, $-0.0015 \pm 0.0000 \text{ } \text{yr}^{-1}$, and $-0.0087 \pm 0.0002 \text{ } \text{yr}^{-1}$ during 1981–
135 2014, respectively. The mean surface pCO₂ trend was somewhat smaller than the growth of
136 atmospheric CO₂, which was at a mean rate of $1.68 \text{ } \mu\text{atm yr}^{-1}$ over the same period. Large spatial
137 variability was evident in the modeled trends (Figures 1a–1c; Table S1), suggesting that local
138 processes were influencing the long-term changes. The largest departures from the basin-averaged
139 values were located near the MARS delta, in the central part of the northern GoM shelf, where
140 negative pCO₂ trends and positive Ω_{Ar} and pH trends were obtained nearshore. As a result, the
141 average trend on the northern GoM inner shelf (bottom depth < 25 m; Figure 1f) was 0.93 ± 0.10
142 $\mu\text{atm yr}^{-1}$, $-0.0009 \pm 0.0001 \text{ } \text{yr}^{-1}$ and $-0.0003 \pm 0.0009 \text{ } \text{yr}^{-1}$ for pCO₂, pH and Ω_{Ar}, respectively,
143 the slowest rates compared to those in other shelves and the open GoM. The modeled long-term
144 changes in surface pCO₂ impacted the air-sea CO₂ flux (Figure 1d, Table S1). The most prominent
145 feature was on the northern GoM inner shelf, where the CO₂ flux trend was strongly negative
146 (increase in carbon uptake), averaging $-0.018 \pm 0.003 \text{ mol m}^{-2} \text{ yr}^{-2}$ for a mean flux of -0.844 mol
147 $\text{m}^{-2} \text{ yr}^{-1}$, but reaching maximum trend magnitude rates greater than $-0.050 \text{ mol m}^{-2} \text{ yr}^{-2}$ near the
148 MARS delta. The basin-averaged flux trend was $-0.004 \pm 0.001 \text{ mol m}^{-2} \text{ yr}^{-2}$ for a model mean
149 flux of $-0.382 \text{ mol m}^2 \text{ yr}^{-1}$.

150 Changes in surface pCO₂, pH, and Ω_{Ar} are connected to changes in DIC, TA, salinity, and
151 temperature. Both pH and Ω_{Ar} increase with TA and decrease with DIC and salinity. However,
152 their response to temperature differs, as warming decreases calcium carbonate solubility
153 (increasing Ω_{Ar}) but promotes hydrogen ion formation (decreasing pH). pCO₂ displays the opposite
154 pattern to that of pH, increasing with DIC, salinity, and temperature, and decreasing with TA. A
155 potential reason for the small pCO₂, pH, and Ω_{Ar} trends on the northern GoM shelf could be an
156 increased biological uptake of DIC that counteracts the DIC increase due to anthropogenic CO₂.
157 However, the simulated surface net community production—the difference between phytoplankton
158 production and community respiration—displayed a weak negative trend near the MARS delta,
159 linked to decreased river discharge and nutrient runoff (Figure 1e). Consequently, a biologically
160 driven offset of the modeled OA trends was discarded.

161 To identify processes responsible for the simulated OA pattern, we examined the Taylor
162 decomposition of the pCO₂, pH, and Ω_{Ar} trends. The patterns showed that sDIC, which had a basin-

163 averaged growth of $1.16 \pm 0.02 \mu\text{mol kg}^{-1} \text{yr}^{-1}$, dominated the total trend variability (Figures 2a–
164 2c; Figure 3a; Table S1). The greatest sDIC impact was on the northern GoM inner shelf, where
165 the sDIC trend was 1.7 times the basin value. This implied that the slow OA progression in the
166 region was not driven by sDIC. Instead, the main process responsible for the slow acidification
167 was a significant sTA growth of $1.90 \pm 0.22 \mu\text{mol kg}^{-1} \text{yr}^{-1}$, which largely counteracted the sDIC-
168 induced changes (Figures 2d–2f; Figure 3b; Table S1). The contributions of SSS and SST to the
169 pCO₂, pH, and Ω_{Ar} trends were relatively minor (Figures 2g–2l). The salinity increase, which
170 averaged 0.007 yr^{-1} over the GoM basin and reached values greater than 0.020 yr^{-1} over the
171 northern GoM shelf and the southern part of the West Florida shelf (Figure 3c; Table S1),
172 strengthened the OA pattern. Surface warming, which was $0.008 \pm 0.002^\circ\text{C yr}^{-1}$ on average across
173 the GoM basin (Figure 3d; Table S1), contributed to increase the magnitude of the pH and pCO₂
174 trends, and had a weak positive impact on Ω_{Ar}. Although small in magnitude, the SSS and SST-
175 induced changes influenced the spatial OA pattern. If we removed the SSS and SST contribution
176 from the total trends, a smoother trend pattern was obtained (Figure S1).

177 The trend decomposition revealed that sTA played a key role as driver of the simulated OA
178 trends around the MARS delta. Strong sTA growth on the northern GoM shelf, as well as the
179 enhanced sDIC trend, could be linked to changes in MARS chemistry. This was evident when we
180 compared the low-frequency TA and DIC changes for the MARS and the surface northern GoM
181 shelf waters (Figure S2). The TA and DIC from the MARS increased about 5 and 3 $\mu\text{mol kg}^{-1} \text{yr}^{-1}$
182 during 1981–2014, respectively (Table S2). Declining trends in river discharge ($-67 \pm 54 \text{ m}^3 \text{s}^{-1}$
183 yr^{-1} for the MARS; $-53 \pm 19 \text{ m}^3 \text{s}^{-1} \text{yr}^{-1}$ for rivers other than MARS) could also contribute to the
184 nearshore sTA and sDIC increase. This is because most rivers along the northern GoM coast,
185 excluding those in the southern and central Texas coast, have relatively low TA and DIC
186 concentration compared to the ocean values; thus, a decreasing discharge implies a reduced
187 influence of the river’s dilution effect on these two variables. To quantify the influence of rivers
188 on the ocean carbonate system, we examined the patterns derived from the CLM_RIV and
189 CLM_MC experiments and compared them with the model hindcast. Over the northern GoM shelf,
190 CLM_RIV showed that changes in river discharge and MARS chemistry accounted for 84% of the
191 hindcast sTA trend and 40% of the hindcast sDIC trend (Figures 3e and 3f; Table S3). Over the
192 same region, CLM_MC showed that the MARS chemistry changes (excluding river flow changes)
193 accounted for 61% of the hindcast sTA trend and 32% of the hindcast sDIC trend (Figures S3a and

194 S3b; Table S3). Consequently, changes in river discharge (CLM_MC minus CLM_RIV)
 195 accounted for 23% and 8% of the hindcast's TA and DIC trends, respectively (Figures S3e and
 196 S3f). Although the sTA trend substantially decreased in the CLM_RIV experiment, a residual TA
 197 trend remained across the basin, consistent with a positive trend in SSS (Figure 3g). This sTA and
 198 SSS variation, connected to variability in the boundary conditions and a negative trend in
 199 precipitation minus evaporation (Figure S4), largely vanished in the CLM_FORC experiment
 200 (Figures 3j and 3k).

201 On the northern GoM shelf, the average OA indicators trends in the climatological
 202 experiments displayed the same sign than in the hindcast run but with a greater magnitude (Figure
 203 4; Table S3). River runoff had a much stronger impact on Ω_{Ar} than on pCO₂ or pH. This was mostly
 204 related to the variable's sensitivity to changes in TA and DIC. Ω_{Ar} is slightly more responsive to
 205 changes in TA than DIC, whereas pCO₂ and pH are more responsive to changes in DIC than TA
 206 (Table S4). Consequently, the DIC-driven changes counteracted to a greater degree the TA-driven
 207 changes in the cases of pCO₂ and pH. For other coastal regions and the open GoM, the
 208 climatological experiments produced relatively weak trend changes in the OA indicators. At the
 209 basin level, the effect of river runoff contributed to reduce the pCO₂, pH, and Ω_{Ar} trends by 5%,
 210 6%, and 10%, respectively, while the effect of climate variability contributed to reduce the same
 211 trends by 2%, 3%, and 19%, respectively (Figure S5; Table S3). Note that the removal of the
 212 surface warming trend in the CLM_FORC experiment (Figure 3l) lessened the growth of pCO₂
 213 and the decline of pH, which explained why the strongest pCO₂ and pH trends were obtained by
 214 CLM_RIV rather than CLM_FORC.

215 4 Discussion

216 High-resolution ocean models are valuable tools to describe OA trends, particularly in the
 217 absence of long-term carbon chemistry time-series. In open GoM waters, our model outputs
 218 showed surface trends of $1.59 \pm 0.02 \mu\text{atm yr}^{-1}$, $-0.0016 \pm 0.0000 \text{yr}^{-1}$, and $-0.0093 \pm 0.0001 \text{yr}^{-1}$
 219 for the mean pCO₂, pH, and Ω_{Ar} anomalies from 1981-2014, respectively. These values are close
 220 to previous estimations for subtropical waters in the North Atlantic (Table S5). Along the coastal
 221 margins of the GoM, our model revealed significant variations in the OA trend. Estimated shelf
 222 averages for the four shelves (Figure 1f) ranged from 1.31 to $1.70 \mu\text{atm yr}^{-1}$ for pCO₂, from $-$
 223 0.0013 to -0.0017yr^{-1} for pH, and from -0.0042 to -0.0094yr^{-1} for Ω_{Ar} . For 1996-2018, Kealoha

et al. (2020) reported mean pCO₂ trends of $3.20 \pm 1.47 \mu\text{atm yr}^{-1}$ and $0.08 \pm 1.66 \mu\text{atm yr}^{-1}$ on the western and central parts of the northern GoM shelf, and $2.35 \pm 0.82 \mu\text{atm yr}^{-1}$ on the West Florida shelf. The large trend discrepancies between their estimates and ours are most likely due to the limited spatiotemporal coverage of the pCO₂ datasets used by Kealoha et al. (2020), mostly based on underway ship measurements. This limited coverage, added to the large interannual carbon chemistry variability driven by the MARS runoff, determined a large uncertainty to their long-term trend calculations. This also applies to the very strong pCO₂ trend reported in Robbins et al. (2018) for the West Florida shelf ($4.37 \mu\text{atm yr}^{-1}$).

Although it is expected that CO₂ in the ocean follows the atmospheric CO₂ growth, multiple studies have shown differences between the ocean and atmospheric CO₂ trends, as interannual and interdecadal variability can exert a significant impact on the ocean sink and pCO₂ trend trajectories (McKinley et al., 2020; Bates & Johnson, 2020). Our model results showed that the basin-averaged pCO₂ trend for 1981-2014 was 7% smaller than the historic atmospheric CO₂ trend. Once we removed the effect associated with river runoff in the CLM_RIV experiment, the difference was insignificant (1%). The positive sTA trend had a significant impact on the three OA indicators examined, contributing to lessen OA progression. The largest sTA increase was on the northern GoM shelf associated with MARS chemistry changes, but the model also exhibited positive sTA trends over the open GoM that were not connected to the coastal sTA signature. This result was consistent with observational studies documenting significant alkalinity growth in the subtropical north Atlantic during the last decades (Bates et al., 2014; Bates & Johnson, 2020; Fine et al., 2017). Besides the sTA growth, the model simulated positive trends for SSS and SST. Surface pCO₂ and pH were especially sensitive to SST changes, with surface warming contributing to accentuate the pCO₂ and pH magnitude in trends.

The MARS is a key driver of hydrographic and biogeochemical patterns on the northern GoM shelf. Multiple studies have reported its influence on salinity, coastal circulation, plankton production, nutrients, dissolved oxygen, and carbon chemistry (e.g., Dagg & Breed, 2003; Rabalais et al., 2007; Lohrenz et al., 2012; Huang et al., 2015). Our study adds another aspect to the impact of the MARS runoff, showing that increasing trends in the river alkalinity had a strong buffering effect nearshore. A sensitivity analysis using climatological forced experiments indicated that changes in MARS chemistry accounted for a 42% reduction in the mean surface Ω_{Ar} trend magnitude over the northern GoM shelf. Changes in river discharge further reduced this Ω_{Ar} trend

255 magnitude by 8%. Although the potential for watershed export changes to counteract OA patterns
256 has been long recognized (Provoost et al., 2010; Duarte et al., 2013; Montagna et al., 2018),
257 previous OA studies on the northern GoM shelf have mainly focused on the link between coastal
258 eutrophication and subsurface acidification (e.g., Cai et al., 2011), disregarding the effect of
259 riverine alkalinity changes. Quantifying river runoff impacts on OA trends is difficult due to the
260 lack of observations to describe historical river chemistry changes. We could only prescribe time-
261 evolving TA, DIC, and nutrients concentration for the MARS, which accounts for 80% of the total
262 river discharge in the northern GoM, and climatological TA, DIC, and nutrients for other rivers.
263 Thus, the potential impacts linked to secular chemistry changes in small rivers have not been
264 accurately represented. Although acidification has been suggested for Texas rivers (Hu et al.,
265 2015) several studies have shown that the dominant pattern for the U.S. rivers is alkalinization,
266 linked to agriculture practices such as changes in water fluxes and liming (e.g., Raymond et al.,
267 2008; Kaushal et al., 2013; Stets et al., 2014). Therefore, we could expect that carbon-chemistry
268 trends in small rivers would mostly contribute to strengthening, at a local scale, the simulated sTA
269 trend driven by MARS runoff.

270 **5 Conclusions**

271 Our model results showed significant long-term changes in carbon system patterns across
272 the GoM mainly driven by an increase in atmospheric CO₂. The simulated basin-average patterns
273 in the open GoM were consistent with observational studies of OA in subtropical North Atlantic
274 waters. However, a slow OA progression was found on the northern GoM shelf, associated with a
275 significant increase in sTA. The large sTA trend over the northern GoM shelf was mainly due to
276 a positive trend in MARS alkalinity, and secondarily due to the declining discharge trends of low
277 alkalinity rivers. Our study shows the interplay of multiple processes influencing carbon system
278 variability.

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286 **Data Availability Statement**

287 The model outputs used in this study are provided as supplementary information for peer review
288 purposes. Model outputs will be made available in a NOAA repository. The USGS datasets, the
289 ERA-interim reanalysis product, and the atmospheric CO₂ time-series at Mauna Loa Observatory
290 were obtained at <https://waterdata.usgs.gov/nwis/inventory/>,
291 <https://apps.ecmwf.int/datasets/data/interim-full-daily/levtype=sfc/>; and
292 https://gml.noaa.gov/webdata/ccgg/trends/co2/co2_mm_mlo.txt, respectively.

293 **References**

- 294 Bates, N. R., Astor, Y. M., Church, M. J., Currie, K., Dore, J. E., González-Dávila, M., et al.
295 (2014). A time-series view of changing ocean chemistry due to ocean uptake of anthropogenic
296 CO₂ and ocean acidification. *Oceanography*, 27(1): 126–141.
- 297 Bates, N. R., & Johnson, R. J. (2020). Acceleration of ocean warming, salinification,
298 deoxygenation and acidification in the surface subtropical North Atlantic
299 Ocean. *Communications Earth & Environment*, 1(1), 1–12.
- 300 Busch, D. S., Bennett-Mintz, J. M., Armstrong, C. T., Jewett, E. B., Gledhill, D. K., & Ombres, E.
301 H. (2018). NOAA Ocean Acidification Program: Taking Stock and Looking Forward, A
302 summary of the 2017 Principal Investigators' Meeting. U.S. Dept. of Commerce, *NOAA*
303 *Technical Memorandum OAR-OAP-1*, 50 p.
- 304 Cai, W. J., Hu, X., Huang, W. J., Murrell, M. C., Lehrter, J. C., Lohrenz, S. E., et al. (2011).
305 Acidification of subsurface coastal waters enhanced by eutrophication. *Nature geoscience*,
306 4(11), 766–770.
- 307 Cross, J. N., Turner, J. A., Cooley, S. R., Newton, J. A., Azetsu-Scott, K., Chambers, R. C., et al.
308 (2019). The Knowledge-to-Action Pipeline: Connecting Ocean Acidification Research and
309 Actionable Decision Support. *Frontiers in Marine Science*, 6, p.356.
- 310 Dagg, M. J. & Breed, G. A. (2003). Biological effects of Mississippi River nitrogen on the northern
311 Gulf of Mexico—a review and synthesis. *J. Mar. Syst.*, 43(3-4), 133–152.
- 312 Damien, P., Pasqueron de Fommervault, O., Sheinbaum, J., Jouanno, J., Camacho-Ibar, V. F., &

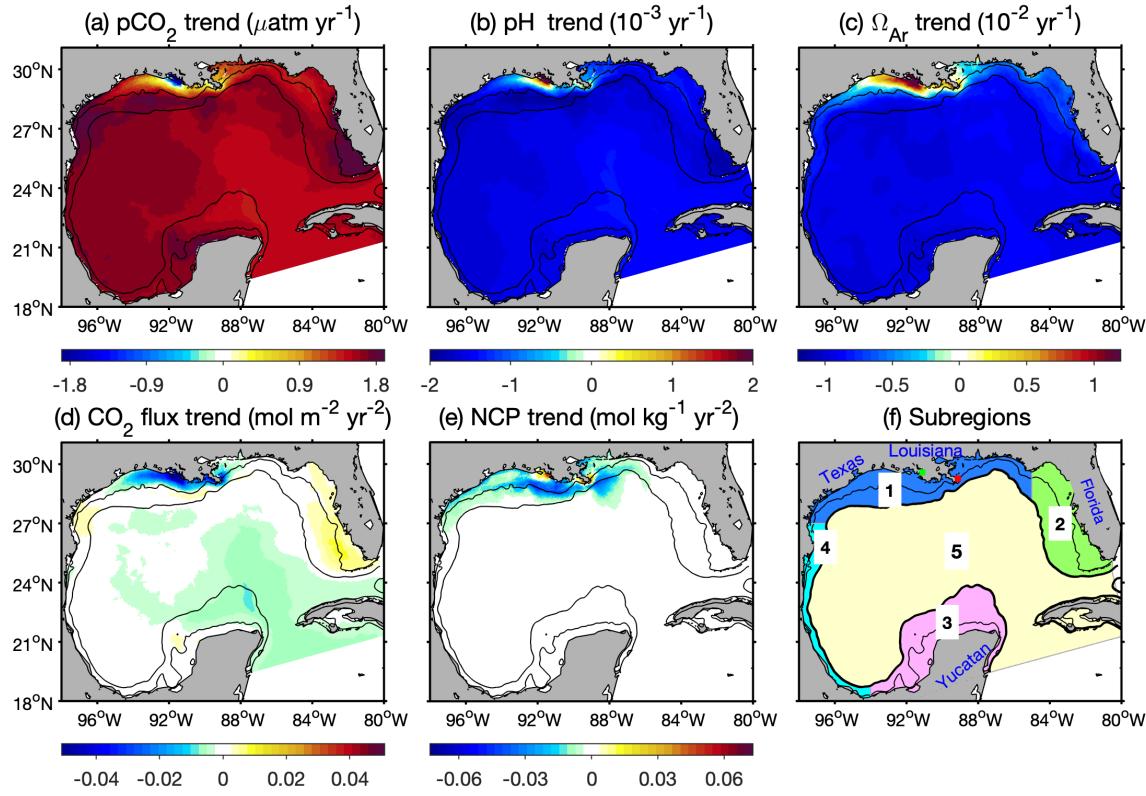
- 313 Duteil, O. (2018). Partitioning of the open waters of the Gulf of Mexico based on the seasonal
314 and interannual variability of chlorophyll concentration. *J. Geophys. Res.-Oceans*, 123(4),
315 2592–2614.
- 316 Dee, D. P., Uppala, S. M., Simmons, A. J., Berrisford, P., Poli, P., Kobayashi, S., et al. (2011).
317 The ERA-Interim reanalysis: configuration and performance of the data assimilation system.
318 *Q. J. Roy. Meteor. Soc.*, 137, 553–597.
- 319 Doney, S. C., Busch, D. S., Cooley, S. R., & Kroeker, K. J. (2020). The Impacts of Ocean
320 Acidification on Marine Ecosystems and Reliant Human Communities. *Annual Review of
321 Environment and Resources*, 45:83–112.
- 322 Doney, S. C., Fabry, V. J., Feely, R. A., & Kleypas, J. A. (2009). Ocean acidification: the other
323 CO₂ problem. *Annu. Rev. Mar. Sci.*, 1, 169–92.
- 324 Duarte, C. M., Hendriks, I. E., Moore, T. S., Olsen, Y. S., Steckbauer, A., Ramajo, L., et al. (2013).
325 Is ocean acidification an open-ocean syndrome? Understanding anthropogenic impacts on
326 seawater pH. *Estuaries and Coasts*, 36(2), 221–236.
- 327 Ekstrom, J. A., Suatoni, L., Cooley, S. R., Pendleton, L. H., Waldbusser, G. G., Cinner, J. E., et
328 al. (2015). Vulnerability and adaptation of US shellfisheries to ocean acidification. *Nature
329 Climate Change*, 5(3), 207–214.
- 330 Fine, R. A., Willey, D. A., & Millero, F. J. (2017). Global variability and changes in ocean total
331 alkalinity from Aquarius satellite data. *Geophysical Research Letters*, 44(1), 261–267.
- 332 Gledhill, D. K., Wanninkhof, R., Millero, F. J., & Eakin, M. (2008). Ocean acidification of the
333 greater Caribbean region 1996–2006. *J. Geophys. Res.-Oceans*, 113(C10).
- 334 Gomez, F. A., Lee, S. K., Liu, Y., Hernandez Jr, F. J., Muller-Karger, F. E., & Lamkin, J.
335 T. (2018). Seasonal patterns in phytoplankton biomass across the northern and deep Gulf of
336 Mexico: a numerical model study, *Biogeosciences*, 15, 3561–3576.
- 337 Gomez, F. A., Wanninkhof, R., Barbero, L., Lee, S. K., & Hernandez, F. J. (2020). Seasonal
338 patterns of surface inorganic carbon system variables in the Gulf of Mexico inferred from a
339 regional high-resolution ocean biogeochemical model, *Biogeosciences*, 17, 1685–1700.
- 340 Gruber, N., Clement, D., Carter, B. R., Feely, R. A., Van Heuven, S., Hoppema, M., et al. (2019).
341 The oceanic sink for anthropogenic CO₂ from 1994 to 2007. *Science*, 363(6432), 1193–1199.
- 342 He, B., Kanae, S., Oki, T., Hirabayashi, Y., Yamashiki, Y., & Takara, K. (2011). Assessment of
343 global nitrogen pollution in rivers using an integrated biogeochemical modeling framework.

- 344 *Water Res.*, 45, 2573–2586.
- 345 Hoegh-Guldberg, O., Mumby, P. J., Hooten, A. J., Steneck, R. S., Greenfield, P., Gomez, E., et al.
346 (2007). Coral reefs under rapid climate change and ocean acidification. *Science*, 318(5857),
347 1737–1742.
- 348 Hu, X., Nuttall, M. F., Wang, H., Yao, H., Staryk, C. J., McCutcheon, M. R., et al. (2018). Seasonal
349 variability of carbonate chemistry and decadal changes in waters of a marine sanctuary in the
350 Gulf of Mexico. *Marine Chemistry*, 205, 16–28.
- 351 Hu, X., Pollack, J. B., McCutcheon, M. R., Montagna, P. A., & Ouyang, Z. (2015). Long-term
352 alkalinity decrease and acidification of estuaries in northwestern Gulf of Mexico.
353 *Environmental science & technology*, 49(6), 3401–3409.
- 354 Huang, W. J., Cai, W. J., Wang, Y., Lohrenz, S. E., & Murrell, M. C. (2015). The carbon dioxide
355 system on the Mississippi River-dominated continental shelf in the northern Gulf of Mexico:
356 1. Distribution and air-sea CO₂ flux. *J. Geophys. Res.-Oceans*, 120(3), 1429–1445.
- 357 Kaushal, S. S., Likens, G. E., Utz, R. M., Pace, M. L., Grese, M., & Yepsen, M. (2013). Increased
358 river alkalinization in the Eastern US. *Environmental science & technology*, 47(18), 10302–
359 10311.
- 360 Kealoha, A. K., Shamberger, K. E., DiMarco, S. F., Thyng, K. M., Hetland, R. D., Manzello, D.
361 P., et al. (2020). Surface Water CO₂ variability in the Gulf of Mexico (1996–2017). *Scientific
362 reports*, 10(1), 1–13.
- 363 Laruelle, G. G., Cai, W. J., Hu, X., Gruber, N., Mackenzie, F. T., & Regnier, P. (2018). Continental
364 shelves as a variable but increasing global sink for atmospheric carbon dioxide. *Nature
365 communications*, 9, 454.
- 366 Lauvset, S. K., Gruber, N., Landschützer, P., Olsen, A., & Tjiputra, J. F. Trends and drivers in
367 global surface ocean pH over the past 3 decades. *Biogeosciences*, 12(5), 1285–1298 (2015).
- 368 Liu, Y., Lee, S. K., Enfield, D. B., Muhling, B. A., Lamkin, J. T., Muller-Karger, F. E., & Roffer,
369 M. A. (2015). Potential impact of climate change on the Intra-Americas Sea: Part-1, A dynamic
370 downscaling of the CMIP5 model projections. *J. Mar. Syst.*, 148, 56–69.
- 371 Lohrenz, S. E., Cai, W. J., Chakraborty, S., Huang, W. J., Guo, X., He, R., et al. (2018). Satellite
372 estimation of coastal pCO₂ and air-sea flux of carbon dioxide in the northern Gulf of Mexico,
373 *Remote Sens. Environ.*, 207, 71–83.
- 374 Lohrenz, S. E., Cai, W. J., Chen, F., Chen, X., & Tuel, M. (2010). Seasonal variability in air-sea

- 375 fluxes of CO₂ in a river influenced coastal margin. *J. Geophys. Res.-Oceans*, 115, C10034.
- 376 Martínez-López, B., & Zavala-Hidalgo, J. (2009). Seasonal and interannual variability of cross-
- 377 shelf transports of chlorophyll in the Gulf of Mexico. *J. Mar. Syst.*, 77, 1–20.
- 378 McKinley, G. A., Fay, A. R., Eddebar, Y. A., Gloege, L., & Lovenduski, N. S. (2020). External
- 379 forcing explains recent decadal variability of the ocean carbon sink. *AGU Advances*, 1,
- 380 e2019AV000149.
- 381 Montagna, P. A., Hu, X., Palmer, T. A., & Wetz, M. (2018). Effect of hydrological variability on
- 382 the biogeochemistry of estuaries across a regional climatic gradient. *Limnol. Oceanogr.*, 63(6),
- 383 2465–2478.
- 384 Muller-Karger, F. E., Smith, J. P., Werner, S., Chen, R., Roffer, M., Liu, Y., et al. (2015). Natural
- 385 variability of surface oceanographic conditions in the offshore Gulf of Mexico. *Progress in*
- 386 *Oceanography*, 134, 54–76.
- 387 Muñoz-Salinas, E. & Castillo, M. (2015). Streamflow and sediment load assessment from 1950 to
- 388 2006 in the Usumacinta and Grijalva Rivers (Southern Mexico) and the influence of ENSO.
- 389 *Catena*, 127, 270–278.
- 390 Provoost, P., Van Heuven, S., Soetaert, K., Laane, R. W. P. M., & Middelburg, J. J. (2010).
- 391 Seasonal and long-term changes in pH in the Dutch coastal zone, *Biogeosciences*, 7(11), 3869–
- 392 3878.
- 393 Rabalais, N. N., Turner, R. E., Gupta, B. S., Boesch, D. F., Chapman, P., & Murrell, M. C. (2007).
- 394 Hypoxia in the northern Gulf of Mexico: Does the science support the plan to reduce, mitigate,
- 395 and control hypoxia?. *Estuaries and Coasts*, 30(5), 753–772.
- 396 Raymond, P. A., Oh, N. H., Turner, R. E., & Broussard, W. (2008). Anthropogenically enhanced
- 397 fluxes of water and carbon from the Mississippi River. *Nature*, 451(7177), 449–452.
- 398 Robbins, L. L., Daly, K. L., Barbero, L., Wanninkhof, R., He, R., Zong, H., et al. (2018). Spatial
- 399 and temporal variability of pCO₂, carbon fluxes and saturation state on the West Florida Shelf.
- 400 *J. Geophys. Res.-Oceans*, 123.
- 401 Salisbury, J. E., & Jönsson, B. F. (2018). Rapid warming and salinity changes in the Gulf of Maine
- 402 alter surface ocean carbonate parameters and hide ocean acidification. *Biogeochemistry*,
- 403 141(3), 401–418.
- 404 Shchepetkin, A. F., & McWilliams, J. C. (2005). The regional oceanic modeling system (ROMS):
- 405 a split-explicit, free-surface, topography-following-coordinate oceanic model. *Ocean Model.*,

- 406 9, 347–404.
- 407 Stets, E. G., Kelly, V. J., & Crawford, C. G. (2014). Long-term trends in alkalinity in large rivers
408 of the conterminous US in relation to acidification, agriculture, and hydrologic modification.
409 *Sci. Total Environ.*, 488, 280–289.
- 410 Turi, G., Lachkar, Z., Gruber, N., & Münnich, M. (2016). Climatic modulation of recent trends in
411 ocean acidification in the California Current System, *Environmental Research Letters*, 11(1),
412 p.014007.
- 413 van Heuven, S. M. A. C., Pierrot, D., Rae, J. W. B., Lewis E., & Wallace D. W. R. (2011).
414 MATLAB program developed for CO₂ system calculations. ORNL/CDIAC-105b. Carbon
415 Dioxide Information Analysis Center, Oak Ridge National Laboratory, US Department of
416 Energy, Oak Ridge, Tennessee, 530.
- 417 Waldbusser, G. G., Hales, B., Langdon, C. J., Haley, B. A., Schrader, P., Brunner, E. L., et al.
418 (2015). Saturation-state sensitivity of marine bivalve larvae to ocean acidification. *Nature
419 Climate Change*, 5(3), 273–280.
- 420 Wang, Z. A., Wanninkhof, R., Cai, W. J., Byrne, R. H., Hu, X., Peng, T. H., & Huang, W. J.
421 (2013). The marine inorganic carbon system along the Gulf of Mexico and Atlantic coasts of
422 the United States: Insights from a transregional coastal carbon study. *Limnol. Oceanogr.*, 58,
423 325–342.
- 424 Wanninkhof, R., Barbero, L., Byrne, R., Cai, W. J., Huang, W. J., Zhang, J. Z., et al. (2015). Ocean
425 acidification along the Gulf Coast and East Coast of the USA. *Continental Shelf Research*, 98,
426 54–71.
- 427 Wanninkhof, R., Trinanes, J., Park, G.-H., Gledhill, D., & Olsen, A. (2019). Large decadal changes
428 in air-sea CO₂ fluxes in the Caribbean Sea. *Journal of Geophysical Research: Oceans*, 124,
429 6960–6982, <https://doi.org/10.1029/2019JC015366>
- 430 Xu, Y. Y., Cai, W. J., Wanninkhof, R., Salisbury, J., Reimer, J., & Chen, B. (2020). Long-term
431 changes of carbonate chemistry variables along the north American East Coast. *J. Geophys.
432 Res.-Oceans: Oceans*, 125(7), 2019JC015982.

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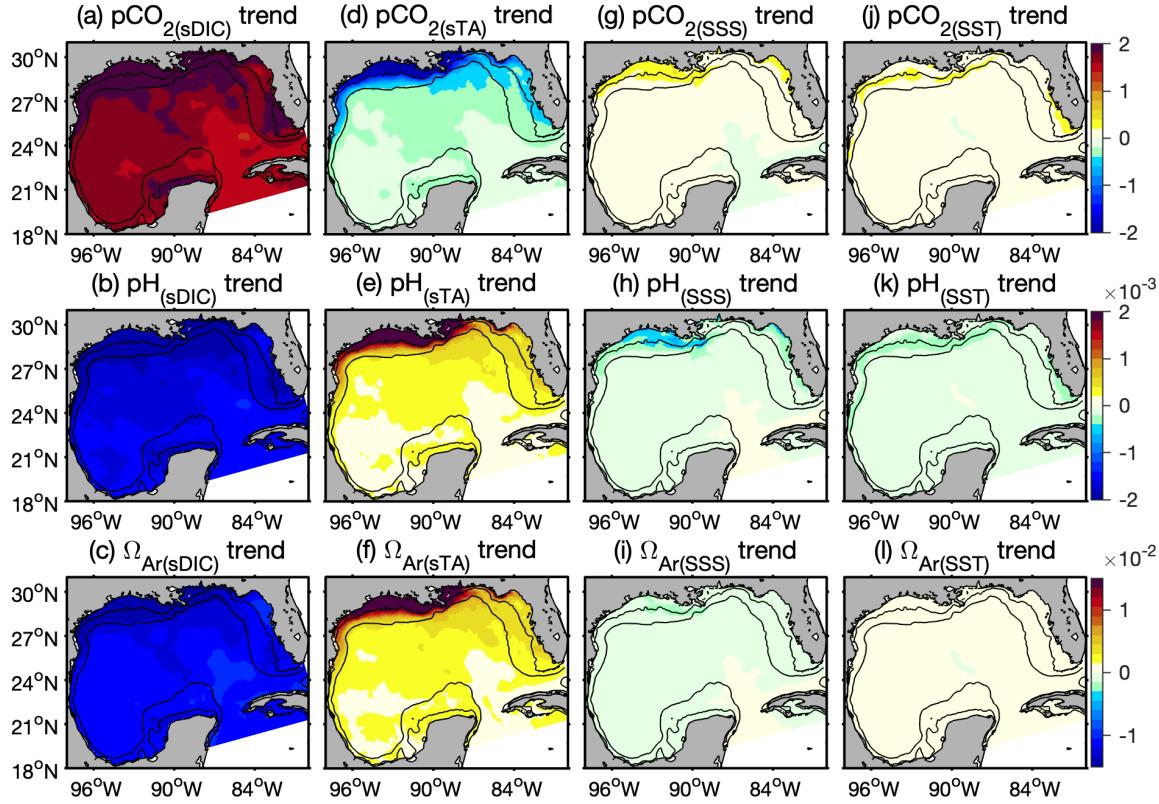
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435 **Figure 1.** Surface trends of (a) partial pressure of CO_2 , (b) pH, c) aragonite saturation state, (d)
 436 air-sea CO_2 flux, and (e) net community production derived from the model hindcast. (f) Areas
 437 used to derive subregional trend patterns: (1) northern GoM shelf; (2) West Florida shelf; (3)
 438 Yucatan shelf; (4) western GoM shelf; and (5) open GoM. Red and green dots in (f) depict the
 439 Mississippi and Atchafalaya mouths, respectively. Negative CO_2 flux trend implies increasing
 440 carbon uptake. Black contours depict the 25 and 200 m isobaths. The 25 m isobath defines the
 441 limit between the inner and outer shelf.

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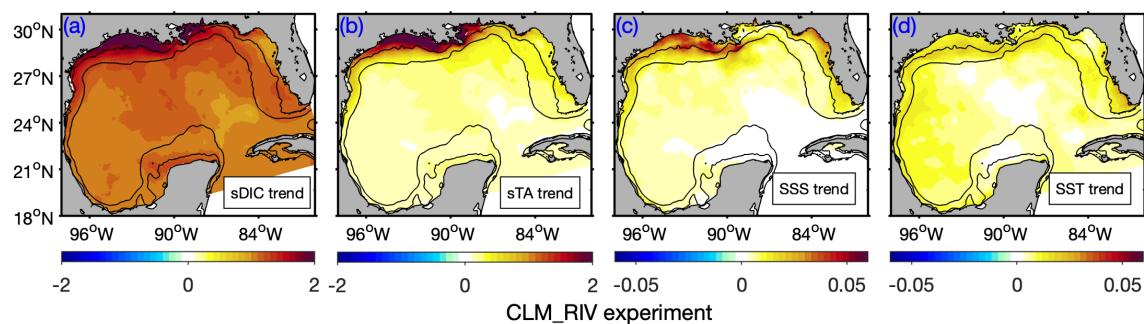
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445 **Figure 2.** Taylor series decomposition of the surface partial pressure of CO₂ ($\mu\text{atm yr}^{-1}$; upper
 446 panels), surface pH (yr^{-1} ; middle panels), and surface aragonite saturation state (yr^{-1} ; bottom
 447 panels) trends derived from the model hindcast. Patterns terms represent the contribution of (a–c)
 448 surface dissolved inorganic carbon (sDIC); (d–f) surface total alkalinity (sTA); (g–i) sea surface
 449 salinity (SSS); and (j–l) sea surface temperature (SST). Black contours depict the 25 and 200 m
 450 isobaths.

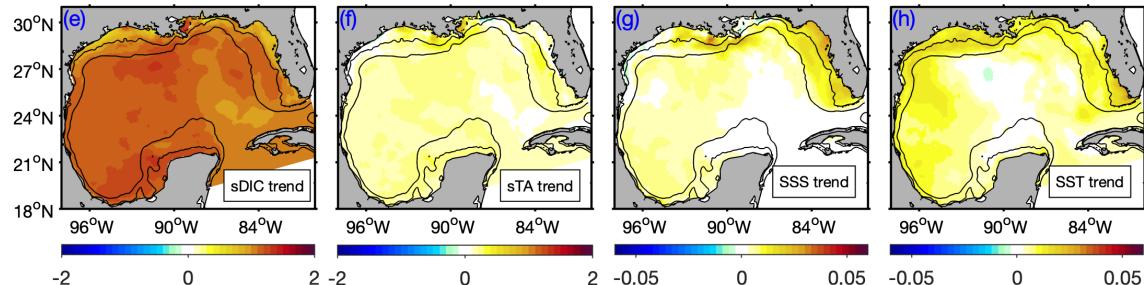
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Hindcast experiment



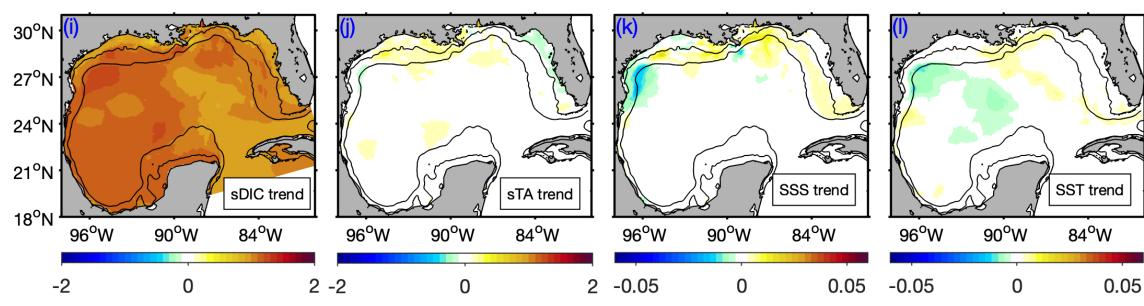
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CLM_RIV experiment



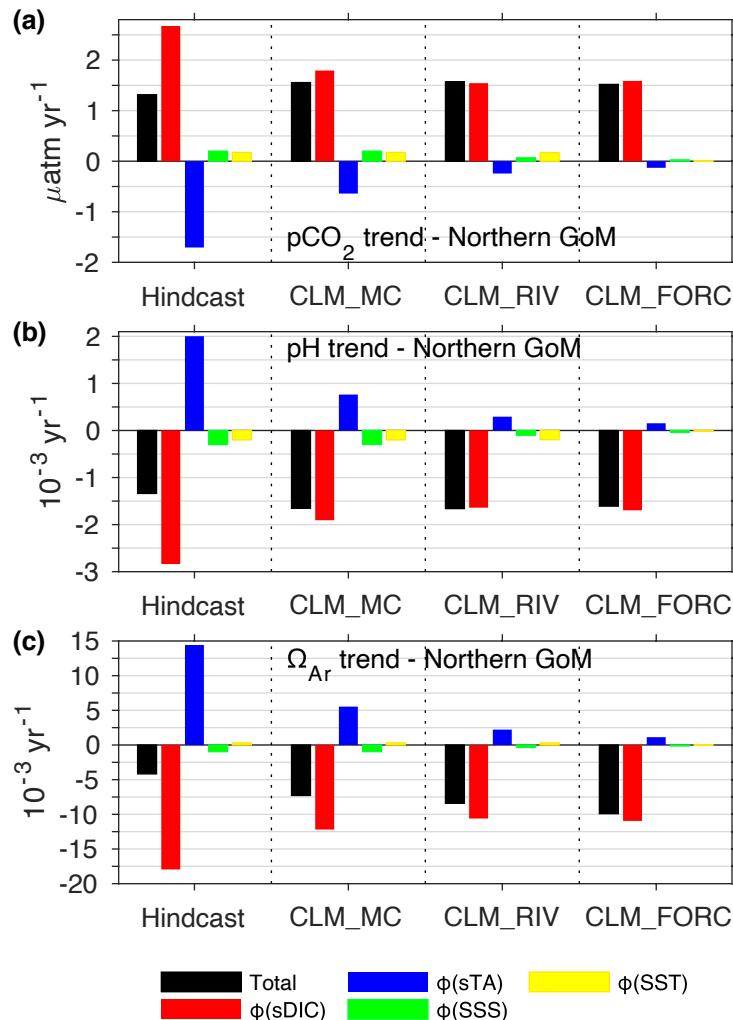
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CLM_FORC experiment



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Figure 3. Trends of surface dissolved inorganic carbon (sDIC), surface total alkalinity (sTA), sea surface salinity (SSS), and sea surface temperature (SST) as derived from the (a–d) hindcast, (e–h) climatological rivers (CLM_RIV), and (i–l) climatological forcing (CLM_FORC) experiments. Trends for sDIC and sTA are in $\mu\text{mol kg}^{-1} \text{yr}^{-1}$, for SSS in yr^{-1} , and for SST in $^{\circ}\text{C yr}^{-1}$. Black contours depict the 25 and 200 m isobaths.



459

460 **Figure 4.** Trend decomposition of ocean acidification indicators over the northern GoM shelf
 461 derived from the hindcast, CLM_MC, CLM_RIV, and CLM_FORC experiments: **(a)** partial
 462 pressure of CO_2 ($p\text{CO}_2$), **(b)** pH, and **(c)** aragonite saturation state (Ω_{Ar}). Red, blue, green, and
 463 yellow bars represent the contribution of surface dissolved inorganic carbon (sDIC), surface total
 464 alkalinity (sTA), sea surface salinity (SSS), and sea surface temperature (SST) to the total trend
 465 (in black), respectively.