Supplementary Material for Updated climatological mean delta fCO_2 and net sea–air CO_2 flux over the global open ocean regions

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Supplementary

Here we discuss the method and results based on observations included in the LDEOv2019 database to create an updated climatology. Comparisons are also made to the climatology discussed in the main text which is based on the SOCATv2022 database.

Methods

LDEO database

The LDEOv2019 database (available at https://www.ncei.noaa.gov/access/ ocean-carbon-acidification-data-system/oceans/LDEO_Underway_Database/, Takahashi et al. (2020)) consists of over 14 million measurements of pCO_2^{oce} with the earliest observations dating back to 1957 and the most recent collected in 2019 (Supplementary Figure 1). This database includes only pCO_2^{oce} values measured directly using the air–water equilibration method and requires that two or more standard gas mixtures were used for analyzer calibrations. This strict criteria for observation quality is unique to the LDEO database.

In this analysis, we restrict the time period to include observations collected beginning in 1980, which accounts for 99.9% of the available observations within the LDEOv2019 database. Additionally, we eliminate observations in the database that are not accompanied by both an observed sea surface temperature (SST) and atmospheric sea level pressure (SLP). Not only does this act to flag observations that might not be of the highest quality, it also allows a consistent methodology for creating the climatology from both the LDEO and SOCAT databases since the ancillary observations of SST and SLP are necessary to convert from pCO_2 to fCO_2, as well as to calculate a delta value, both steps which are essential in this updated climatology version.

Within the LDEO database, there are approximately 9400 observations without SST observations and nearly 755,000 missing SLP. Given instances where both SST and SLP are missing, the total number of omitted observations with this criteria is 764,115. Approximately 13.4 of the 14 million observations in the LDEO database meet all ancillary data requirements.

We have converted all pCO_2 observations in the LDEO database to fCO_2 values. As a pre-processing step, we have calculated fCO_2 values at the reported SST which helps to ensure a uniform representation of the surface ocean observations. The protocol for this conversion step follows that of the SOCAT methodology (Pfeil et al. 2013) which utilizes the equations recommended by Dickson et al. (2007) and requires observed temperature, salinity, and pressure.

Given the dramatic increase in pCO_2^{oce} measurements available since previous releases of the climatology (LDEOv2006, T-2009, and LDEOv2012, T-2014, included nearly 3 and 6.5 million observations, respectively, covering years 1970 to 2007 and 1957 to 2012, respectively), we do not remove the observations collected in the equatorial Pacific during El Niño years since inclusion does not strongly influence the overall result as in previous versions where those data made up a larger percentage of available observations.

There is a large overlap between the LDEO and SOCAT databases particularly for data prior to circa 2015. The LDEO and SOCAT databases are similar in that they restrict the included data to only observations that are measured in near-continuous operation or in discrete samples with an equilibrator system. Neither database includes pCO_2/fCO_2 measurements that are calculated from dissolved inorganic carbon, total alkalinity and/or pH.

Atmospheric fCO_2 calculation for LDEO database

For the LDEO database, the corresponding atmospheric CO_2 value is not included in the reported database as it is in the SOCAT database, so atmospheric CO_2 values from the NOAA MBL product (Lan et al. 2023) are matched based on month and location (latitude) of the pCO_2^{oce} observation. In calculating fCO_2 from pCO_2, we use the reported SLP, SST and salinity from the LDEO database.

Results

LDEO ΔfCO_2 climatology

Global

Supplementary Figure 2 shows the near-global annual climatological mean distribution of ΔfCO_2 (fCO_2^{oce} minus fCO_2^{air}) for both databases. Large-scale patterns across the global ocean incluce the consistent high (positive) ΔfCO_2 values in the equatorial Pacific where upwelling is a dominant influence, and low (negative) values of ΔfCO_2 in the North Atlantic physical processes including evaporation (increase salinity) and cooling drive strong uptake of carbon and subduction of surface waters.

As for SOCAT, the near-global LDEO ΔfCO_2 climatology curve has a bimodal shape (Supplementary Figure 3) with a smaller peak in boreal spring (March/April) and a larger peak in late boreal summer (August/September). The LDEO curve reaches its minimum in January and begins a recovery throughout the boreal winter before dipping again for a springtime minimum in May. While the overall pattern is similar between the SOCAT and LDEO curves, the LDEO curve has a larger amplitude, reaching a higher peak and lower trough. The near-global LDEO annual mean ΔfCO_2 value is -3.9 µatm.

Regional

The equatorial regions of the Pacific and Atlantic oceans have positive ΔfCO_2 values throughout the annual cycle and little seasonal variability (Supplementary Figure 3, 4ab). This indicates that these areas are sources of CO_2 to the atmosphere year round. The equatorial Pacific has the highest positive ΔfCO_2 values (annual mean of 31.5 µatm), followed by the tropical Atlantic (annual mean of 11.6 µatm, Supplementary Figure 4).

The subtropical biomes, representing the temperate North and South Atlantic and Pacific basins exhibit large seasonal ΔfCO_2 cycles which change sign throughout the year (Supplementary Figure 4); positive ΔfCO_2 occurs in warm summer months and negative values in colder winter months reflecting the dominance of seasonal temperature changes on the cycles of ΔfCO_2 in these regions. In the LDEO database, the seasonal amplitude for the subtropical North Pacific is 43.3 µatm, and is slightly larger than the seasonal amplitude in the subtropical North Atlantic (39.6 µatm). The same pattern is observed in the SOCAT database however with slightly larger amplitudes for both basins (Figure 4, Supplementary Figure 4). Since the mean seasonal amplitudes for SST are quite similar in these two oceans, with the Atlantic having a slightly larger seasonal change in surface temperature (4.4ºC in Pacific and 5.0ºC in Atlantic), the difference in ΔfCO_2 amplitudes between the Pacific and Atlantic subtropical regions cannot be attributed solely to SST, and may reflect differences in biogeochemical cycling between these two basins.

Seasonal changes in the northern subtropical oceans are roughly six months out of phase from the southern subtropical biomes. The South Pacific subtropical biome has significantly smaller seasonal amplitude than the corresponding Northern Hemisphere region; the South Pacific subtropical biome amplitude is 15.3 µatm. The amplitude in the South Atlantic subtropical basin is much more comparable to the North Atlantic (South Atlantic subtropical amplitude is 37.1 µatm). The Indian Ocean subtropical biome, which encompasses most of the Indian Ocean, both above and below the Equator, has a smaller amplitude (19.8 µatm) but the phasing matches well with the South Pacific and Atlantic biomes, with peak (positive) ΔfCO_2 values in February and the lowest values in August (Supplementary Figure 4). The low fCO_2 in the Indian and South Pacific subtropical basin is partially attributable to lower SST variability in these regions (SST seasonal cycle amplitudes are 4.0ºC in South Pacific and 3.0ºC in the Indian as compared to 4.6ºC in the South Atlantic) however it is likely that differences in spatiotemporal patterns of primary productivity also contribute to this difference. The striking difference in the amplitude of the cycle in the South Pacific and Indian subtropics could also be influenced by undersampling in these basins and in the Southern Hemisphere oceans overall.

The timing of the peak drawdown in the subpolar regions is opposite that observed in the subtropical North Pacific and Atlantic basins. A strong negative ΔfCO_2 in the spring to summer months is due to the effects of biological drawdown which quickly and dramatically lowers the CO_2 levels of the surface ocean. With its biological dependence and strongly stratified mixed layers, the subpolar region seasonal cycle are roughly four to six months out of phase with those from the adjacent subtropical regions. In the Atlantic subpolar biome, ΔfCO_2 values are consistently below zero throughout the annual cycle (maximum of -31.1 µatm occurs in January). In the Pacific basin, the ocean exceeds the atmospheric levels of fCO_2 in the boreal winter (Jan-March) before the spring bloom results in biological drawdown which lowers the ΔfCO_2 values below zero for the remainder of the year. The spring drawdown is weaker in the Pacific basin than the Atlantic.

Supplementary Figure 4c displays the seasonal cycle for the Southern Ocean biomes including the seasonal ice biome, the subpolar region, and the seasonally stratified subtropical region of the Southern Hemisphere. Unlike the subtropical regions of the other basins, this region has a relatively small seasonal ΔfCO_2 amplitude and has consistently negative ΔfCO_2 values (atmosphere>ocean) throughout the annual cycle. The mean of this Southern Ocean subtropical region is -20.9 µatm with a maximum amplitude of 9.1 µatm.

Unlike the seasonally-stratified subtropical region of the Southern Ocean, the Southern Ocean subpolar and ice biomes both have relatively strong seasonal cycles, reaching a maximum ΔfCO_2 of zero or slightly positive during the late austral winter and early austral spring (Supplementary Figure 4).

LDEO flux

The mean annual air-sea CO_2 flux for the LDEO database is -1.68 PgC yr^{-1} with negative indicating an uptake by the ocean. This represents a slightly greater flux into the ocean than the direct estimate from the previous version of the climatology (Takahashi et al. 2009) which estimated global mean flux at 1.4 PgC yr^{-1}. For the uncertainty in global ocean-atmosphere CO_2 flux reported here we use the value reported by Wanninkhof et al. (2013) as described above.

The global mean flux estimate presented here is for the area of the global ocean covered by this database and does not fully extend over the entire global ocean; it covers 90% of the global ocean. Specifically, coastal and high latitude regions are missing also as described above for the SOCAT database.

Supplementary Figure 7 shows the climatological seasonal mean sea–air CO_2 flux (mol m^{-2} yr^{-1}) for two seasons (DJF and JJA). The equatorial Pacific is the most prominent atmospheric CO_2 source region, with a seasonally persistent sea-to-air flux. When combined with the equatorial Atlantic region, the tropical belt emits an annual mean 0.35 PgC yr^{-1} to the atmosphere.

Adjacent to this tropical efflux zone lies an area of seasonally variable uptake patterns. The subtropical basins in both hemispheres act as CO_2 sinks in the cooler months and transition to regions of neutral or small CO_2 sources during the warmer months. At higher subtropical latitudes, strong winds and relatively low ocean fCO_2 occur along the subtropical convergence zone- a region where the cooled subtropical gyre waters with low fCO_2 meet the subpolar waters with biologically-lowered fCO_2.

The Northern Hemisphere subtropical region represents a smaller sink (-0.64 PgC yr^{-1}) than the corresponding Southern Hemisphere region (-0.82 PgC yr^{-1}), largely due to the overall greater size of the oceans in the Southern Hemisphere at these latitudes as noted above. There is also significant uptake in the Southern Ocean subtropical region (-0.55 PgC yr^{-1}).

Comparison of climatologies built from SOCAT and LDEO databases

Global

On a global scale, the monthly mean ΔfCO_2 seasonal amplitudes for the climatology produced using the LDEO database is larger than for the SOCAT database, reaching both higher in the boreal summer and lower in the boreal winter months. The LDEO climatology has an amplitude of 6.6 µatm while the SOCAT global mean climatology amplitude is 5.0 µatm (Supplementary Figure 2).

The mean annual air-sea CO_2 flux resulting from the LDEO version of the climatology created is -1.67 PgC yr^{-1}, with negative value indicating an uptake by the ocean. This represents a slightly greater flux into the ocean than the direct estimate from the previous version of the climatology (T-2009) which estimated global mean flux of -1.4 PgC yr^{-1}. This shift towards greater carbon uptake is consistent with other work indicating increased ocean uptake in recent decades (Friedlingstein et al. 2022, DeVries et al. 2023).

The LDEO climatology annual mean flux is slightly less negative than the mean global air-sea CO_2 flux based on the SOCAT database (-1.79 PgC yr^{-1}). While the overall shape of the seasonal cycle is comparable between the two databases, the amplitude in flux is much larger for the LDEO database, a result of the larger ΔfCO_2 global mean amplitude (Supplementary Figure 2). Specifically, the LDEO database has global mean flux values approaching zero during the boreal summer months, leading to a reduced uptake of carbon during these months. While the boreal winter months have similar flux estimates between the two databases, the difference during the months of July, August, and September ultimately reduce the overall global mean flux value reported from the LDEO database.

Southern Ocean

While the total annual Southern Ocean (<35S) flux estimates are similar (-1.04 PgC yr^{-1} and -0.90 PgC yr^{-1} for SOCAT and LDEO respectively), discrete regions of the Southern Ocean exhibit some of the largest differences in the climatological air-sea flux created from the SOCAT versus LDEO database (Figure 5, Supplementary Figure 6). Specifically, in the ocean region south of Australia, the SOCAT database produces flux estimates of larger carbon uptake/less efflux than the LDEO database. This signal of larger uptake estimates in the SOCAT database is consistent throughout all months of the year but peaks during August, September, and October. These differences are likely a result of more available observations in the SOCAT database in this region (Figure 1, Supplementary Figure 1). Throughout the vast expanse of the remainder of the Southern Hemisphere subtropical and subpolar regions (i.e. the Pacific and Atlantic sectors), the differences are much smaller and heterogeneous (Figure 5, Supplementary Figure 6). Therefore, we do not see substantial biome-scale differences in the climatology of either ΔfCO_2 or carbon flux despite the small anomalous region south of Australia.

North Atlantic Subpolar Differences

For most regions of the global ocean, the ΔfCO_2 climatological cycle is consistent between the SOCAT and LDEO datasets (Figure 4, Supplementary Figure 4). Differences in the absolute magnitude of the ΔfCO_2 values are also observed in the equatorial regions in both the Atlantic and Pacific basins where SOCAT has slightly larger ΔfCO_2 values, but the overall shape and amplitude of the seasonal cycle is consistent between the two databases. One exception to this is the North Atlantic subpolar region where the differences in seasonal climatology between the two datasets are large. The North Atlantic subpolar region has similar total annual ΔfCO_2 estimates (-37.45 μatm and -42.33 μatm for SOCAT and LDEO respectively) but the seasonal differences are profound (Supplementary Figure 9).

The seasonal amplitude in the North Atlantic subpolar biome is over two times as large for the SOCAT database compared to the LDEO database (28.3 μatm in LDEO and 56.9 μatm in SOCAT; Figure 4 and Supplementary Figure 4). While the phasing and shape of the seasonal cycle is consistent between the two databases in this region, there is a significant difference in the amplitude of the winter to summer transition. While the winter (DJF) mean ΔfCO_2 is about 10 μatm different between the two (LDEO being more negative than SOCAT), the opposite is true for the summer season with the SOCAT showing more positive values. The transition to spring and summer blooms, when ΔfCO_2 is greatly reduced allowing for more uptake by the surface ocean, is very different between the two databases with a March to June change of 54.7 µatm in the SOCAT database versus 23.1 µatm for LDEO. Spring/Summer (MAM/JJA) ΔfCO_2 values for the LDEO database are -46.7and -51.6 µatm, respectively, while for the SOCAT database corresponding values are -37.4 and -57.9 µatm, respectively (Figure 4, Supplementary Figures 4 and 9). While an annual mean value in this region may not show a significant difference between the two databases, the differences in seasonal cycle amplitude are likely driven by mechanisms that are more completely captured by the higher sampling density of the SOCAT database and missed in LDEO.

The amplitude of the seasonal cycle increases with time from the 1990s to the 2000s in both databases, however it is the 2010-2019 time period that shows the strongest differences between the climatology produced by each database (Supplementary Figure 9). For the most recent decade (2010-2019), the amplitude of ΔfCO_2 calculated from the LDEO database actually decreases from the previous decade (14.6 µatm) while the amplitude from the SOCAT database is larger than any previous decade, exceeding 50 µatm in absolute amplitude (SOCAT amplitude is 54.8 µatm; Supplementary Figure 9c). The LDEO database is likely lacking sufficient seasonal observations to fully capture the biological drawdown that characterizes this region.

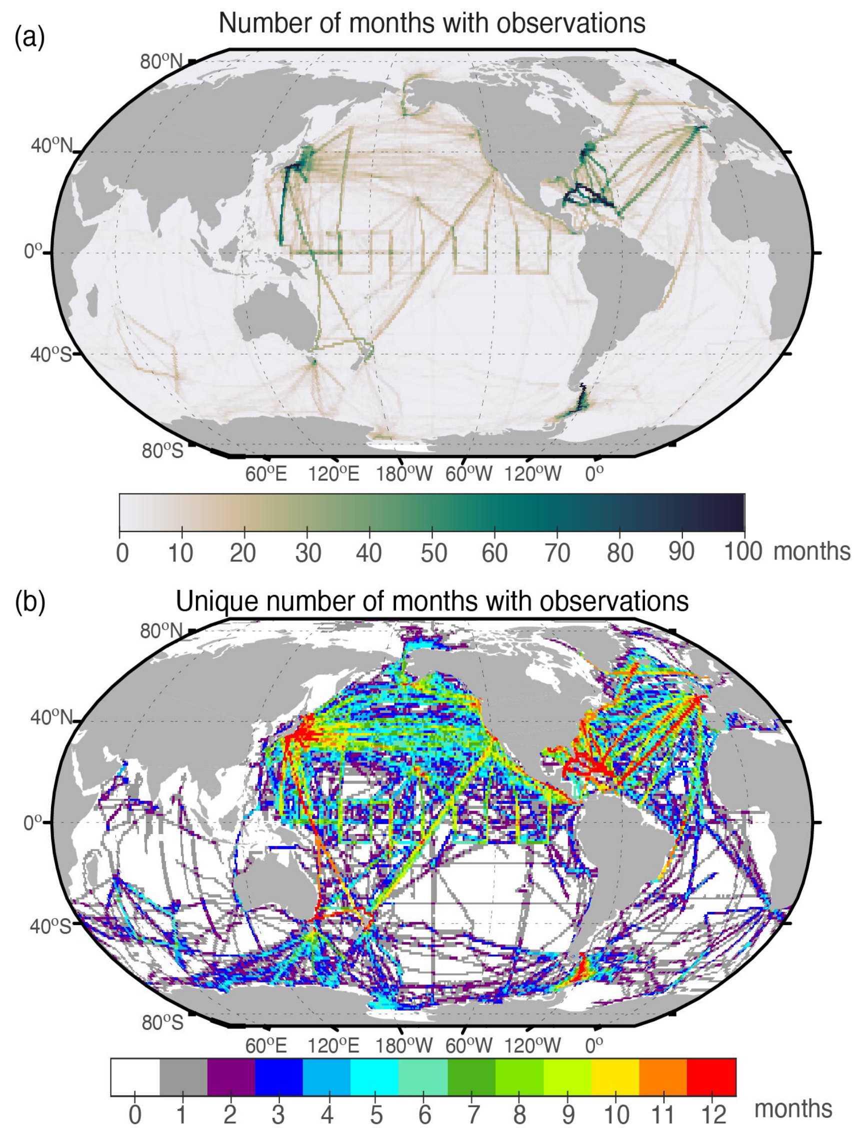
Specifically, this stark contrast is likely due to the abundance of observations in the higher latitudes of the North Atlantic subpolar region in the SOCAT database around Iceland and extending into the Norwegian Sea (Figure 1, Supplementary Figure 1). This result is due both to differences in spatial and temporal coverage. Many grid cells in the version created from the SOCAT database include full seasonal coverage (twelve unique months of observations over the full time period considered). This subpolar North Atlantic is a very dynamic region particularly over the spring/summer months with strong biological drawdown of CO_2 in strongly stratified shallow mixed layers. In order to accurately capture the seasonal evolution of ΔfCO_2, it is imperative to have observations from each season. To capture the evolution of the seasonal cycle in this region over long time intervals requires near continuous full seasonal coverage of observations highlighting the importance of expanded efforts to observe the high latitude oceans.

Supplementary References

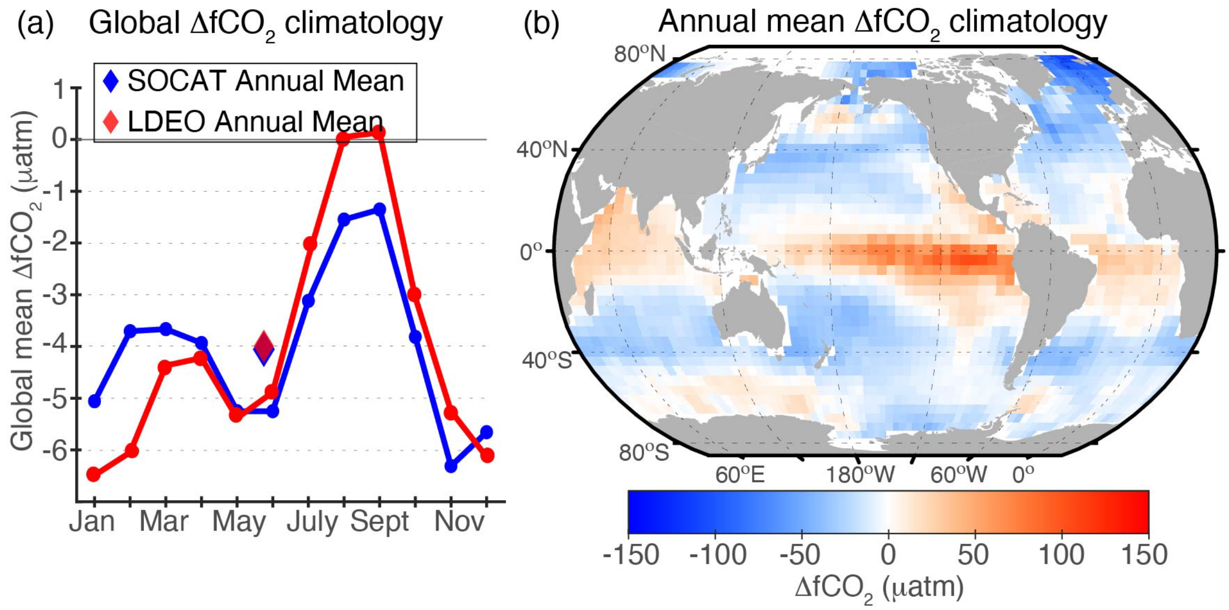
Takahashi, Taro; Sutherland, Stewart C.; Kozyr, Alex (2020). Global Ocean Surface Water Partial Pressure of CO2 Database: Measurements Performed During 1957-2019 (LDEO Database Version 2019) (NCEI Accession 0160492). Version 9.9. NOAA

National Centers for Environmental Information. Dataset. https://doi.org/10.3334/CDIAC/OTG.NDP088(V2015)

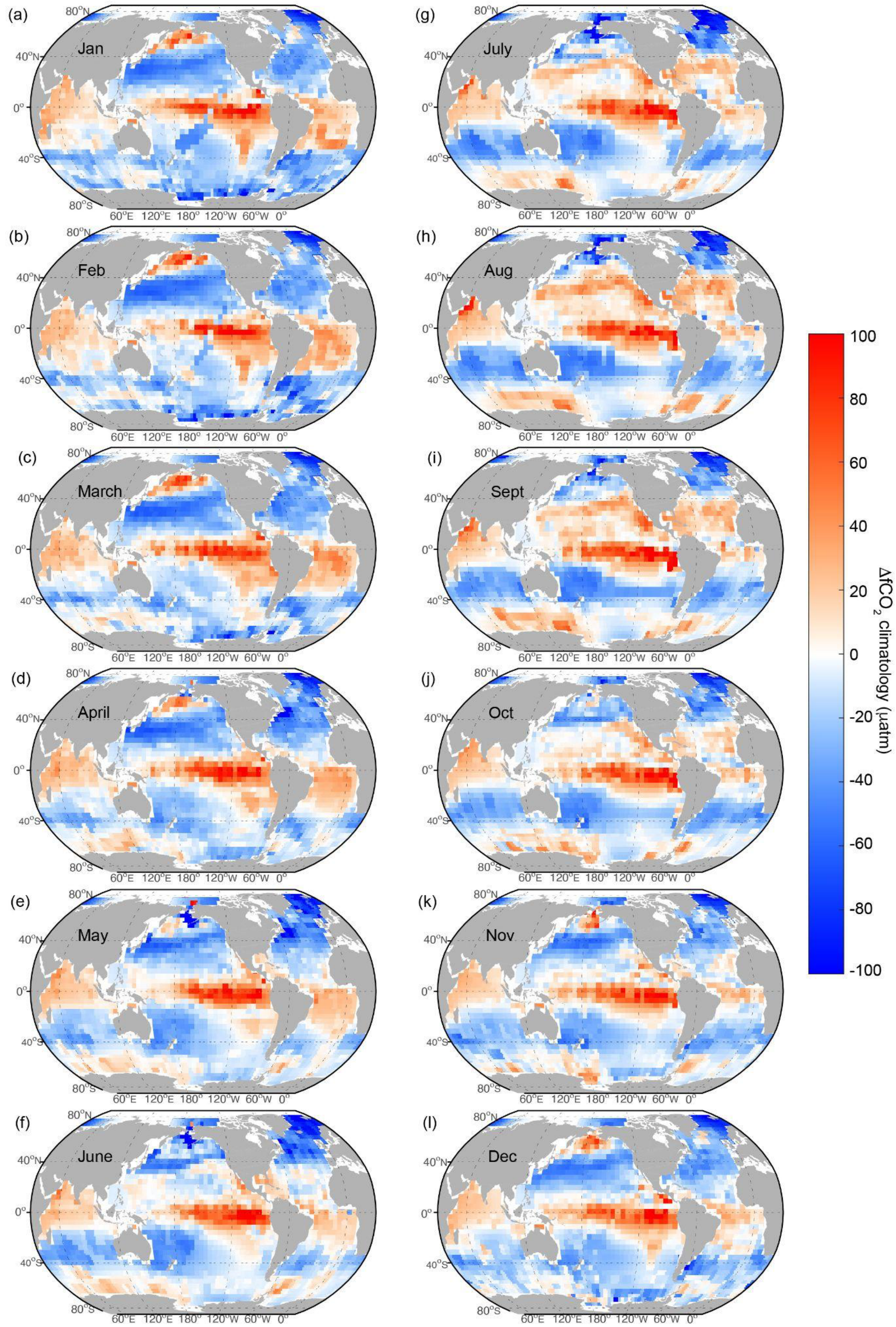
Supplementary Figures



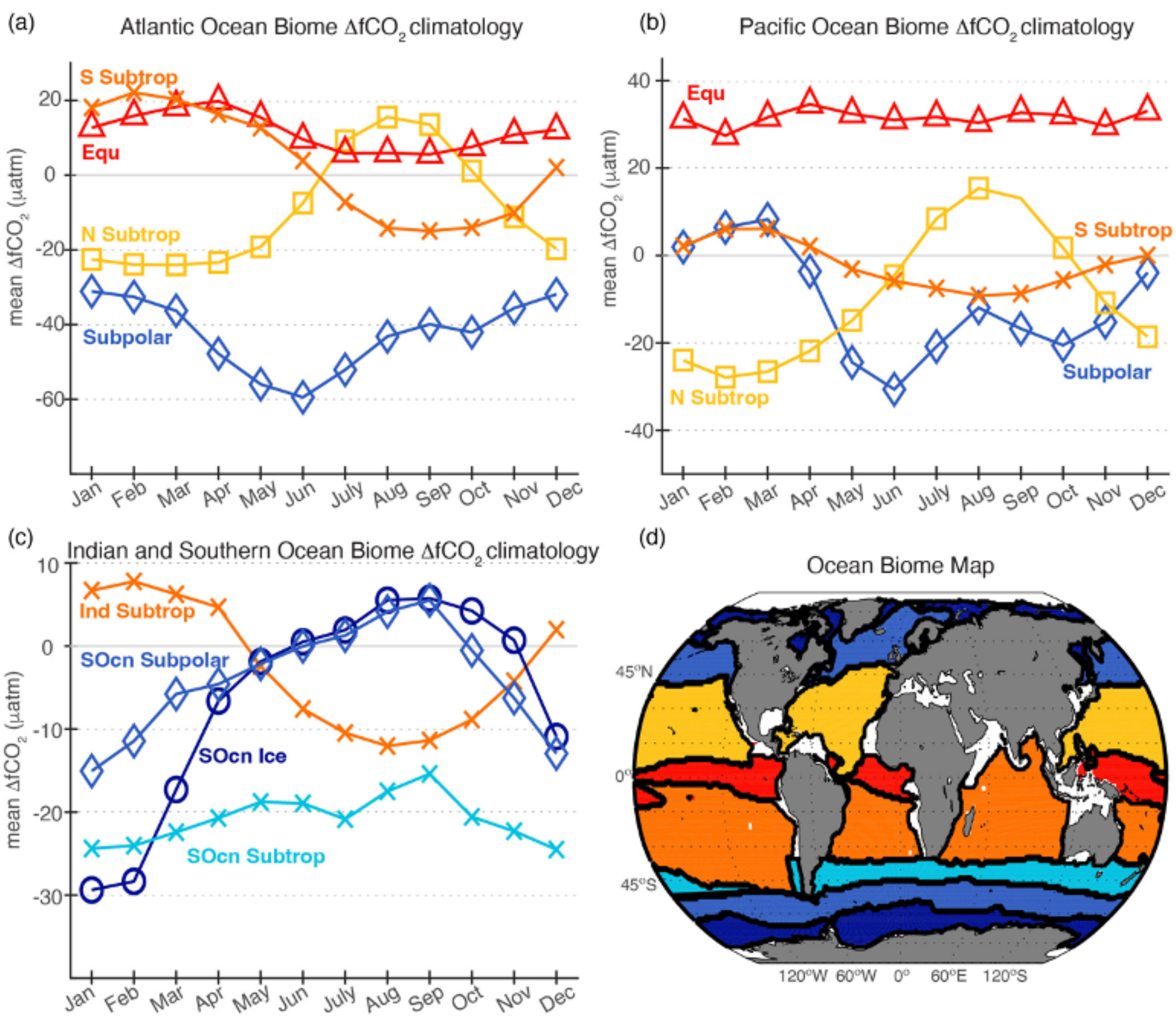
Supplementary Figure 1: (a) Total number of months with at least one observation in each 1º grid cell in the LDEOv2019 database, for years 1980-2019. The maximum number possible for a grid cell is 480 (40 years * 12 months). (b) the number of unique calendar months in each grid cell where at least one observation has been made since 1980. Red indicates grid cells where each month (Jan - Dec) has been sampled at least once over the 40 year time series while white indicates grid cells with no measurements over the length of the time series.



Supplementary Figure 2: (a) Global mean delta fCO_2 seasonal climatology from the SOCATv2022 (blue) and LDEOv2019 (red) databases; annual mean values are indicated by the diamond (SOCATv2022 = -4.1 µatm and LDEOv2019 = -3.9). (b) Map of annual ΔfCO_2 climatology using LDEOv2019 database.



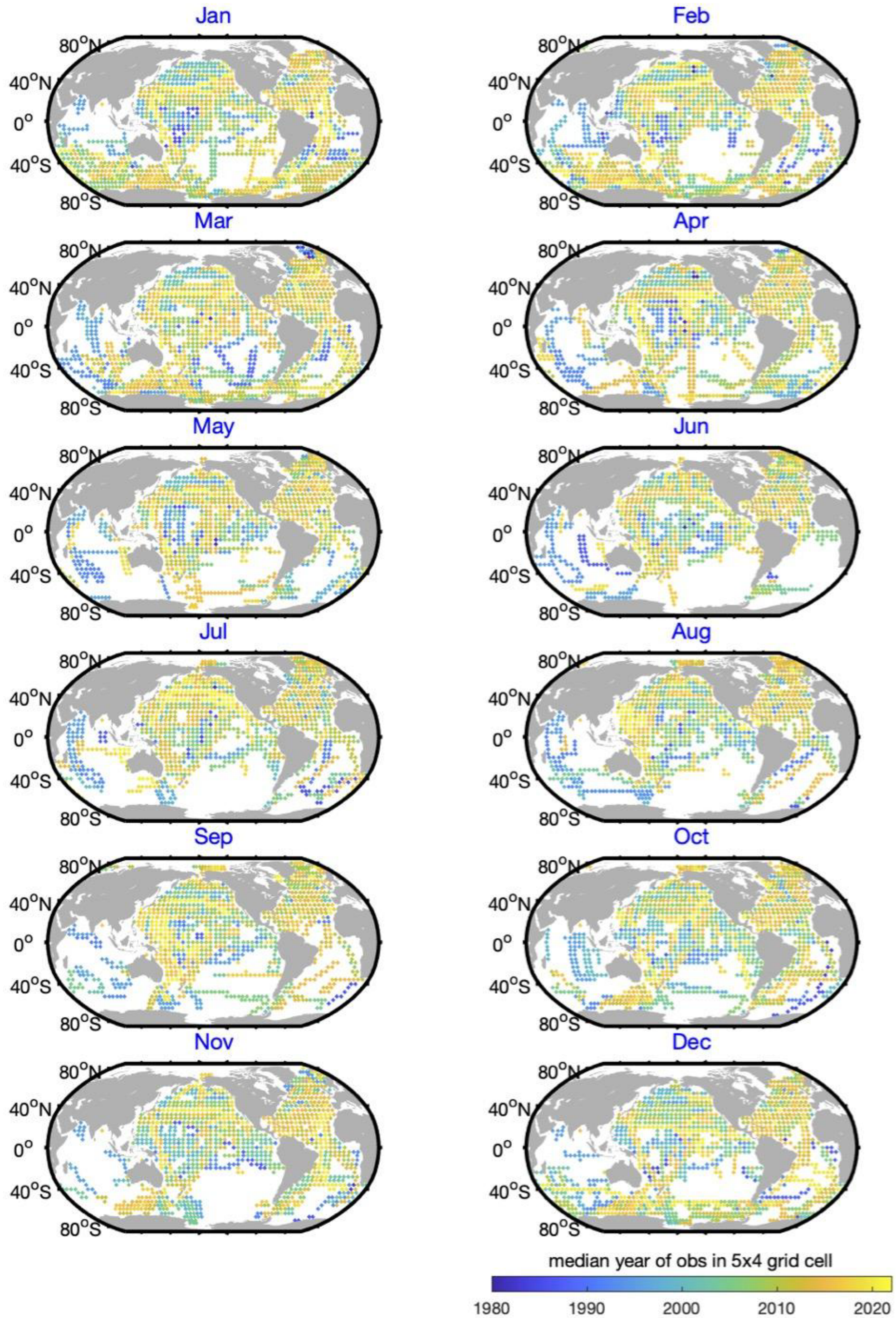
Supplementary Figure 3. Monthly mean values for sea–air ΔfCO_2 obtained using the LDEO database. Warm colors indicate positive ΔfCO_2 (ocean is greater than atmospheric CO_2), white indicates near zero ΔfCO_2, and cool colors indicate negative ΔfCO_2 (ocean CO_2 is lower than the atmosphere).



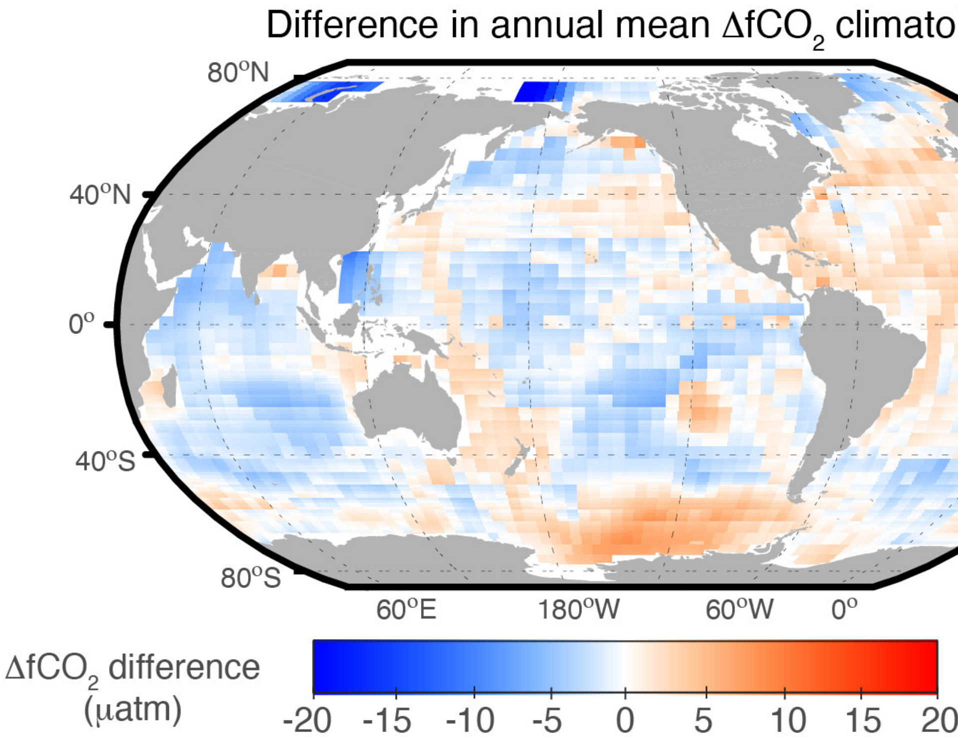
Supplementary Figure 4: Monthly climatology (produced using the LDEO database) of ΔfCO_2 for each regional ocean biome in the (a) Atlantic, (b) Pacific, (c) Indian and Southern Ocean basins. (d) Map of regional biomes. Colors of curves correspond to regions on the map in (d) with labels in matching colored text. Note that the y-axis varies between subplots.

Biome	DJF	MAM	JJA	SON
NP ICE	None (1)	-18.27 (3)	0.64 (20)	1.65 (20)
NP SPSS	2.1 (29)	0.99 (36)	0.94 (38)	1.76 (33)
NP STSS	1.62 (41)	1.38 (37)	1.78 (35)	2.05 (34)
NP STPS	1.49 (41)	1.45 (38)	2.14 (38)	1.94 (36)
W Pac Equ	1.36 (41)	1.38 (34)	1.64 (35)	1.75 (36)
E Pac Equ	2.57 (38)	1.97 (37)	2.04 (34)	2.36 (34)
SP STPS	1.06 (36)	0.54 (36)	0.45 (35)	0.41 (35)
NA ICE	1.38 (12)	0.42 (17)	1.92 (19)	1.82 (20)
NA SPSS	2.02 (27)	1.5 (32)	1.58 (32)	1.28 (31)
NA STSS	1.83 (29)	1.71 (30)	2.08 (31)	1.91 (34)
NA STPS	1.57 (30)	1.59 (28)	2.04 (28)	1.78 (34)
Atl Equ	1.37 (18)	1.49 (23)	1.41 (17)	1.71 (26)
SA STPS	1.69 (24)	1.88 (20)	1.64 (15)	1.58 (27)
IND	1.49 (29)	1.89 (17)	2.23 (17)	1.64 (14)
SO STSS	1.82 (34)	1.69 (32)	1.37 (32)	1.13 (33)
SO SPSS	1.67 (34)	1.77 (32)	1.88 (29)	1.71 (32)
SO ICE	0.87 (33)	1.00 (28)	1.77 (25)	2.64 (29)

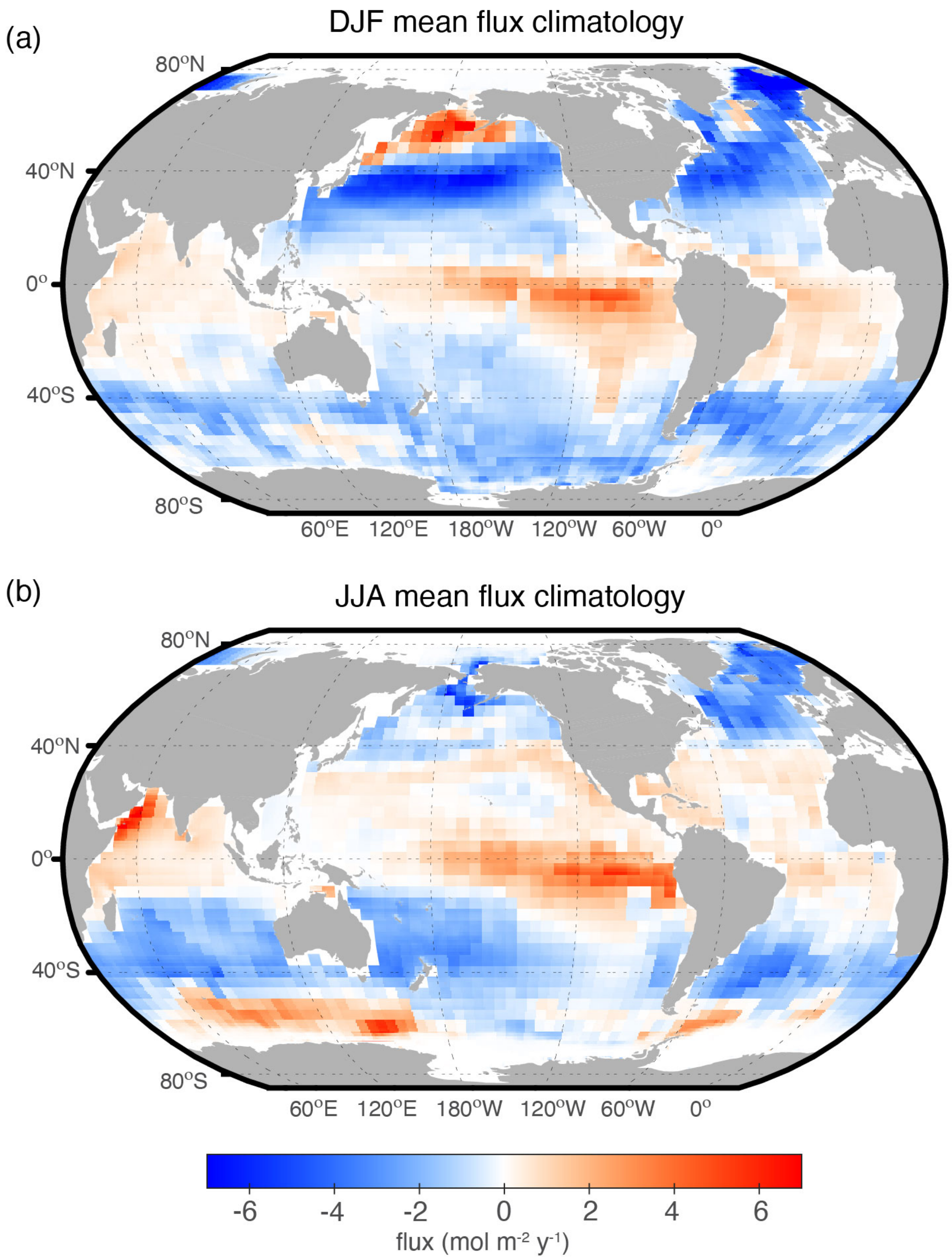
Supplementary Table 1: Seasonal trends for biome-mean fCO_2 values- rows representing the 17 biomes as described in Fay & McKinley et al. 2014 and columns representing seasons (DJF: December, January, February; MAM: March, April, May, etc). Value in parentheses in each cell indicates the number of years with a biome mean value available in that season (max would be 42 as there are 42 years included in our analysis of 1980-2021).



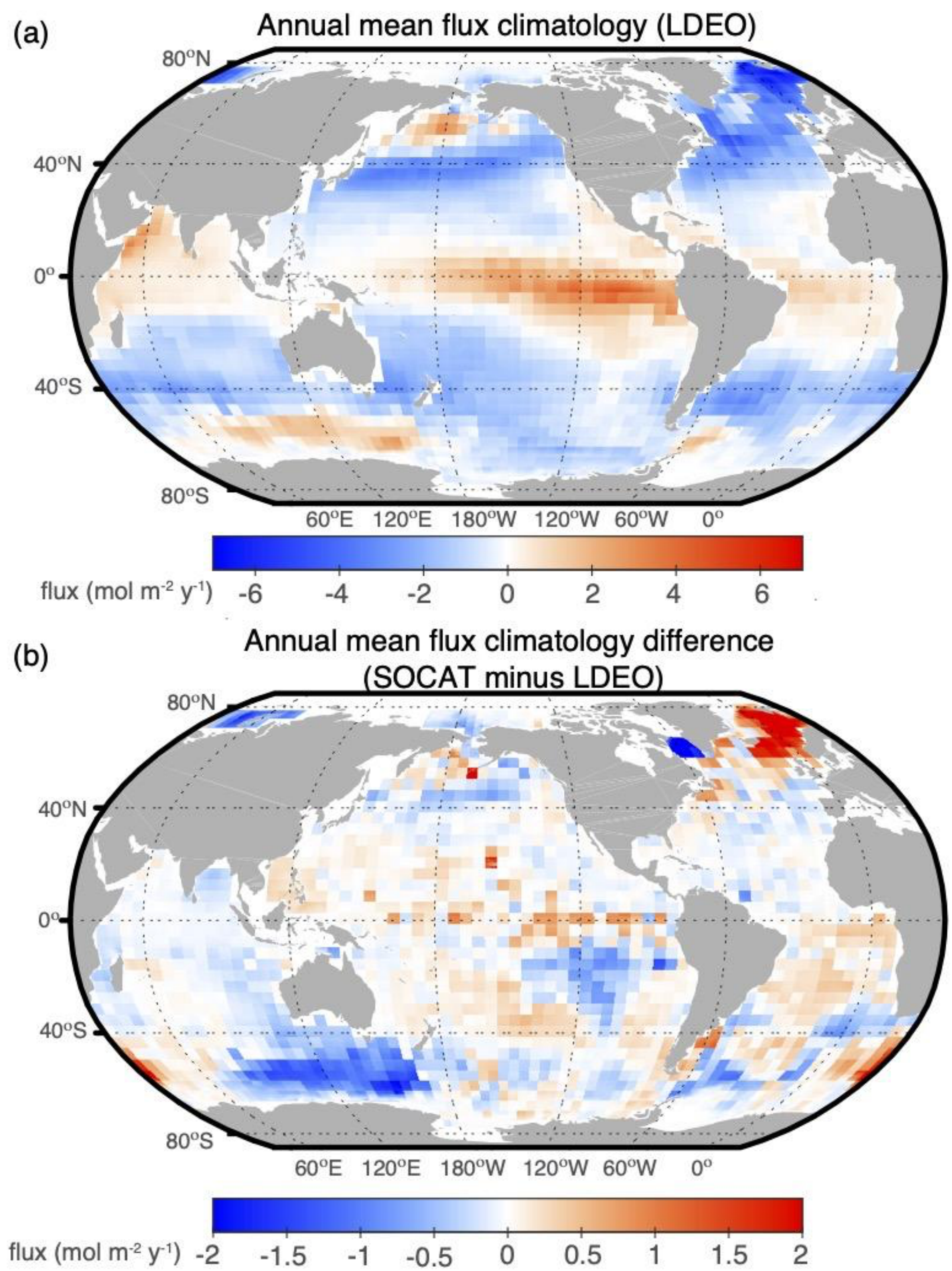
Supplementary Figure 5: Median year of all observations feeding into this climatology, mapped for each month.



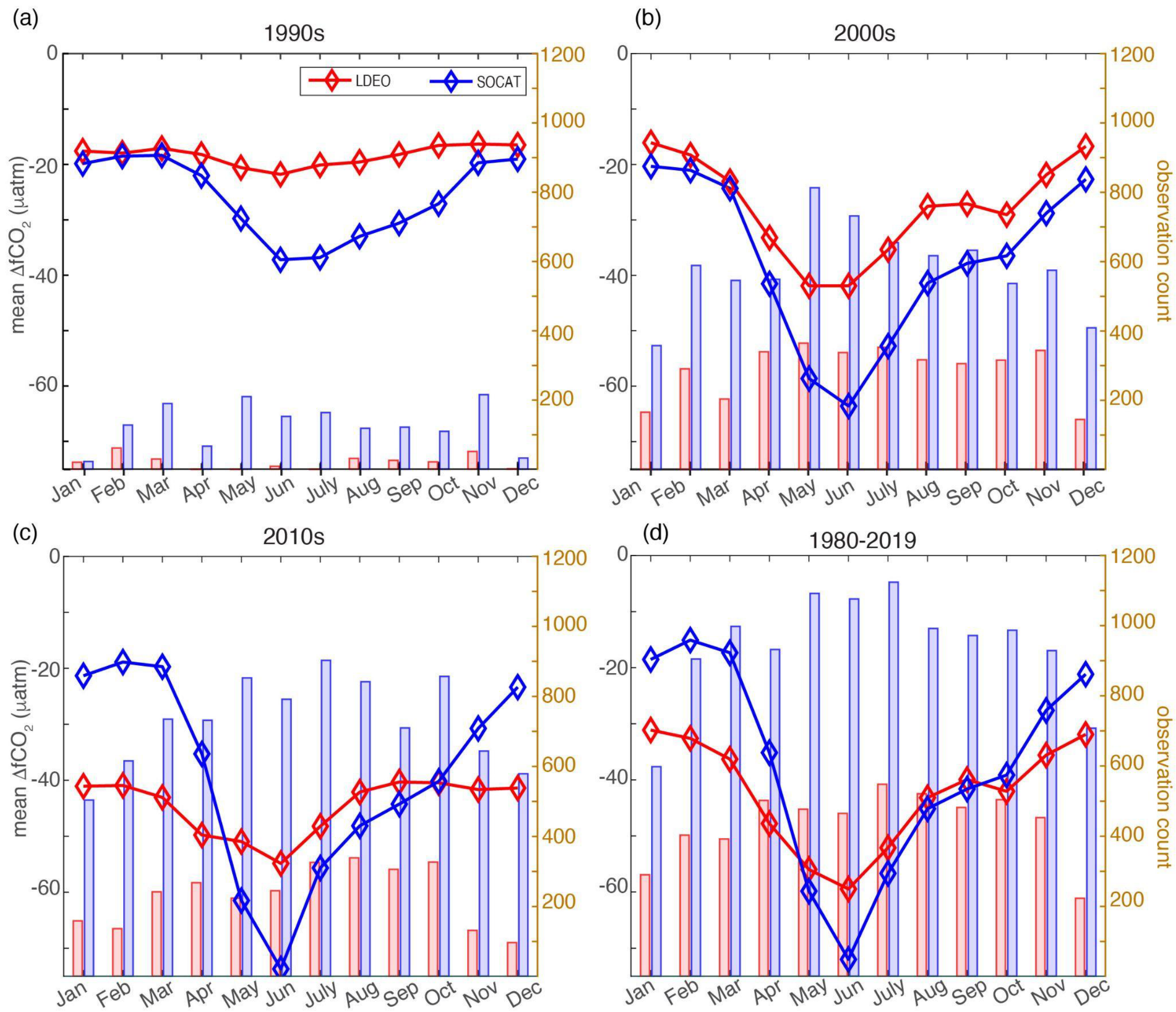
355 Supplementary Figure 6: Annual mean difference in ΔfCO_2 calculated from the SOCAT database using a constant 1.5µatm yr^{-1} time normalization minus the current ΔfCO_2 method.



Supplementary Figure 7: Seasonal sea–air CO_2 flux (mol C m^{-2} $year^{-1}$) climatology for (a) December, January, February (DJF) and (b) June, July, August (JJA) using the LDEO database. Positive values (warm colors) indicate sea-to-air fluxes (ocean efflux), and negative values (cool colors) indicate air-to-sea fluxes (ocean uptake).



Supplementary Figure 8: (a) Annual mean CO_2 flux calculated from the LDEO database and (b) difference in flux between the SOCAT and LDEO database climatologies (SOCAT *minus* LDEO). Flux is calculated identically for each climatology, using the SeaFlux method using the mean of three wind speed reanalysis products. Warm colors indicate regions of carbon efflux and cool colors indicate regions of carbon uptake. The global mean flux is -1.79 PgC yr^{-1} for SOCAT and -1.68 PgC yr^{-1} for LDEO.



Supplementary Figure 9: Monthly mean values for sea-air ΔfCO_2 differences in the North Atlantic Subpolar biome. Average values for each month are plotted for the LDEO database (red) and the SOCAT database (blue) for each decade: (a) 1990-1999, (b) 2000-2009, (c) 2010-2019, and also the full common time period (1980-2019). Bar plots on each subplot show the number of 1ºx1º grid cells in this region which contain observations in the two databases.