Immediate and long-lasting impacts of the Mt. Pinatubo eruption on ocean oxygen and carbon inventories

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Abstract

Large volcanic eruptions drive significant climate perturbations through major anomalies in radiative fluxes and the resulting widespread cooling of the surface and upper ocean. Recent studies suggest that these eruptions also drive important variability in air-sea carbon and oxygen fluxes. By simulating the Earth system using two initial-condition large ensembles, with and without the aerosol forcing associated with the Mt. Pinatubo eruption in June 1991, we isolate the impact of this event on ocean physical and biogeochemical properties. The Mt. Pinatubo eruption generated significant anomalies in surface fluxes and the ocean interior inventories of heat, oxygen, and carbon. Pinatubo-driven changes persist for multiple years in the upper ocean and permanently modify the ocean's heat, oxygen, and carbon inventories. Positive anomalies in oxygen concentrations emerge immediately post-eruption and penetrate into the deep ocean. In contrast, carbon anomalies intensify in the upper ocean over several years post-eruption, and are largely confined to the upper 150 m. In the tropics and northern high latitudes, the change in oxygen is dominated by surface cooling and subsequent ventilation to mid-depths, while the carbon anomaly is associated with solubility changes and eruption-generated ENSO variability. Our results indicate that Pinatubo does not substantially impact oxygen or carbon in the Southern Ocean; forced signals do not emerge from the large internal variability in this region.

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Key Points:

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12	Two initial-condition large ensembles are used to quantify the ocean physical and bio-
13	geochemical response to the 1991 eruption of Mt. Pinatubo
14	• Oxygen is immediately absorbed into the upper ocean and then transits to depth where
15	it permanently increases the interior inventory by 60 Tmol
16	• Mt Pinatubo generated a temporary increase in the ocean carbon sink; a 0.29 ± 0.14 Pg
17	$C \text{ yr}^{-1}$ increase in 1992.

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18 Abstract

Large volcanic eruptions drive significant climate perturbations through major anomalies in 19 radiative fluxes and the resulting widespread cooling of the surface and upper ocean. Recent 20 studies suggest that these eruptions also drive important variability in air-sea carbon and oxy-21 gen fluxes. By simulating the Earth system using two initial-condition large ensembles, with 22 and without the aerosol forcing associated with the Mt. Pinatubo eruption in June 1991, we 23 isolate the impact of this event on ocean physical and biogeochemical properties. The Mt. 24 Pinatubo eruption generated significant anomalies in surface fluxes and the ocean interior in-25 ventories of heat, oxygen, and carbon. Pinatubo-driven changes persist for multiple years in 26 the upper ocean and permanently modify the ocean's heat, oxygen, and carbon inventories. 27 Positive anomalies in oxygen concentrations emerge immediately post-eruption and penetrate 28 into the deep ocean. In contrast, carbon anomalies intensify in the upper ocean over several 29 years post-eruption, and are largely confined to the upper 150 m. In the tropics and northern 30 high latitudes, the change in oxygen is dominated by surface cooling and subsequent ven-31 tilation to mid-depths, while the carbon anomaly is associated with solubility changes and 32 eruption-generated ENSO variability. Our results indicate that Pinatubo does not substan-33 tially impact oxygen or carbon in the Southern Ocean; forced signals do not emerge from the 34 large internal variability in this region. 35

36 Plain Language Summary

The eruption of Pinatubo in June of 1991 produced sunlight-reflecting aerosols in the 37 upper atmosphere and led to a cooling of the planet for several years. While the global cool-38 ing following the eruption is well documented, the impact of the eruption on the ocean oxy-39 gen and carbon budgets has received comparably little attention. As the global ocean oxygen 40 concentration is declining in response to climate change, and as the ocean's continued stor-41 age of anthropogenic carbon is critical for the climate system, it is of interest to quantify the 42 effect of the eruption on both oxygen and carbon in the global ocean. Here, we use an Earth 43 system model to simulate the historical evolution of the climate system both with and with-44 out the Mt. Pinatubo eruption. By comparing the simulations, we are able to quantify the ef-45 fect of the eruption on ocean properties. We find that the eruption led to cooler surface ocean 46 temperatures, and increases in the ocean oxygen and carbon concentrations that persisted for 47 many years. Our simulations can also be used to study other Earth system changes caused by 48 the eruption. 49

50 **1 Introduction**

As a result of anthropogenic activities, the global ocean is losing oxygen and gaining 51 carbon. Observations indicate that the ocean's oxygen inventory has declined by about 2% 52 in the 5 decades following 1960 as the upper ocean warms and stratifies [Ito et al., 2017; 53 Schmidtko et al., 2017]. This oxygen loss has major consequences for nutrient cycling, com-54 pression of marine ecosystem habitats, and global fisheries [Keeling et al., 2010; Gruber, 55 2011; Deutsch et al., 2015]. Since pre-industrial times, the ocean has absorbed ~170 Pg of 56 anthropogenic carbon from the atmosphere [Canadell et al., 2021], which is beneficial for 57 the mitigation of anthropogenic warming, but harmful to some organisms through the related 58 decline in pH, known as ocean acidification. 59

These long-term changes in ocean oxygen and carbon are superimposed on large in-60 terannual to multi-decadal variability, challenging the attribution of reported trends [Long 61 et al., 2016; McKinley et al., 2016; Schlunegger et al., 2020]. Due to their sensitivity to 62 physical and biogeochemical processes, the oceanic oxygen concentrations and air-sea flux 63 exhibit substantial variability across a range of timescales in observations and models [Ito 64 et al., 2010; McKinley et al., 2003; Deutsch et al., 2011; Eddebbar et al., 2017]. Modeling 65 and observation-based studies suggest that both air-sea carbon dioxide flux and ocean car-66 bon concentrations exhibit variability on interannual to multi-decadal timescales [Resplandy 67 et al., 2015; DeVries et al., 2017; Gruber et al., 2019]. Many studies highlight internal cli-68 mate processes and modes of variability (e.g., El Niño - Southern Oscillation, North Atlantic 69 Oscillation, Pacific Decadal Oscillation, Southern Annular Mode) as major drivers control-70 ling variations in the fluxes and inventories of global ocean oxygen and carbon [McKinley 71 et al., 2003, 2004; Lovenduski et al., 2007; Deutsch et al., 2011; Ito and Deutsch, 2013; 72 Landschützer et al., 2016; Eddebbar et al., 2017; McKinley et al., 2017; Landschützer et al., 73 2019; Gruber et al., 2019]. Others suggest an important role for externally driven climate 74 perturbations (e.g., volcanic eruptions) in contributing to these variations [Frölicher et al., 75 2009; Frölicher et al., 2011; Frölicher et al., 2013; Eddebbar et al., 2019; McKinley et al., 76 2020]. It is critical that we develop a fundamental understanding of the drivers of past ocean 77 oxygen and carbon variability so as to allow for clear interpretation of the observational 78 record and also that we can more confidently predict future change. 79

80 81 Despite their well-known influence on global and regional climate [*Marshall et al.*, 2022] and ocean heat uptake [*Gupta and Marshall*, 2018], the impact of volcanic eruptions

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on ocean biogeochemistry is not well quantified. The explosive eruption of the Pinatubo stra-82 tovolcano in the Philippines on 15 June 1991 was the largest in the last 100 years. The vol-83 canic release of sulfur dioxide and subsequent aerosols interaction in the stratosphere led to 84 a substantial scattering of shortwave irradiance and a major reduction in solar heating at the 85 sea surface, driving persistent global and regional changes in climate [Dutton and Christy, 86 1992; Marshall et al., 2022]. The subsequent cooling effect from eruptions of this magnitude 87 have the potential to cause a dramatic, though temporary, pause in global warming trends 88 [Robock and Mao, 1995; Church et al., 2005]. The eruption immediately preceded a boom 89 in ocean observations occurring with the World Ocean Circulation Experiment (WOCE) and 90 Joint Global Ocean Flux Study (JGOFS). Thus, it is possible the impacts from Pinatubo have 91 been imprinted in these observations. 92

Past studies suggest that volcanic-induced climate perturbations can have a profound 93 influence on the oceanic oxygen and carbon distributions and air-sea fluxes. Using a model 94 ensemble, Frölicher et al. [2009] found that volcanic eruptions lead to an increase in interior 95 ocean oxygen concentrations, with volcanic anomalies in oxygen gradually penetrating the 96 top 500 m of the ocean and persisting for several years, but with considerable interannual to 97 decadal variability. However, the small number of ensemble members (3 members) used in 98 their study made regional attribution and process understanding of volcanic effects difficult 99 due to confounding effects of internal (unforced) climate variability. A more recent modeling 100 study leveraged the large number of ensemble members from the Community Earth System 101 Model (CESM) and Geophysical Fluid Dynamics Laboratory model (GFDL) Large Ensem-102 bles (LENS) experiments to explore the volcanic effects from eruptions occurring since 1950 103 [Eddebbar et al., 2019]. They found that tropical eruptions generate strong and spatially de-104 coupled ocean oxygen and carbon uptake, suggesting different processes at play through-105 out the ocean regions. The simulated oceanic oxygen uptake associated with the eruptions 106 of Agung (1963), El Chichon (1982), and Pinatubo (1991) occurred primarily at mid and 107 high latitudes and acted to reduce the magnitude of global ocean deoxygenation due to an-108 thropogenic warming. This study also showcased strong carbon uptake at lower latitudes 109 associated with an El Niño-like response to tropical eruptions in the tropical Pacific that is 110 common across Earth system models [McGregor et al., 2020]. While the large number of 111 ensemble members substantially reduced the confounding influence of internal variability, 112 the combined effect of various external forcings (anthropogenic greenhouse gases, industrial 113

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aerosols, and volcanic aerosols) in this study challenges direct attribution and isolation of
 volcanic eruption effects on prolonged timescales.

In this study, we conduct numerical experiments that isolate the ocean's response to 116 the volcanic forcing, so as to more clearly assess long-term deoxygenation trends and under-117 stand variations in carbon uptake and storage attributable to the Mt. Pinatubo eruption. We 118 quantify the impacts of the Pinatubo eruption on ocean concentrations and air-sea fluxes of 119 oxygen and carbon, and place them into context with anthropogenic forced changes and inter-120 nally driven climate variability. While this paper is limited in scope to an introduction of the 121 model experiments and the examination of oxygen and carbon impacts in the ocean, scien-122 tists throughout the community will find benefit from these runs for understanding the impact 123 of Pinatubo throughout the climate system. 124

Here, the combined analysis of oxygen and carbon changes presents a unique and com-125 plementary perspective on how ocean biogeochemistry and circulation respond to large scale 126 radiative perturbations. Our tool for assessment of the impacts of Pinatubo is a set of large 127 initial condition ensembles of the CESM Large Ensemble experiment, where each ensem-128 ble member has different phasing of internal climate variability. The first ensemble is forced 129 with historical and projected future external forcing, while the second ensemble is forced 130 identically with the sole exception that it excludes the aerosols due to the Pinatubo eruption. 131 This experimental protocol permits a clean separation of the climate and biogeochemical im-132 pacts of the Pinatubo eruption on the Earth system. 133

First we will introduce the model setup experiments for this work. In section 3, we 134 evaluate the global mean and spatial patterns of the difference between these two ensembles 135 for SST, oxygen and carbon air-sea exchanges and inventories. We consider these as indica-136 tors of the impact of the eruption on the ocean's physical and biogeochemical state. In sec-137 tion 4, we discuss the mechanisms behind these changes, relationships to climate modes, and 138 consider comparisons to observations and previous modeling work on the topic. Thoughts 139 on the direction for future work are also included here. We conclude in section 5 with a sum-140 mary of our results. 141

142 **2 Methods**

¹⁴³ To generate an initial-condition large ensemble, a climate model is run multiple times ¹⁴⁴ under identical forcing, but with very small perturbations in initial conditions. These per-

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turbations evolve naturally and amplify rapidly, such that each ensemble member follows a 145 unique climate trajectory through the phase space. The external forcing response, associated 146 with the shared identical external forcing, is isolated in the mean across ensembles. Within 147 the framework of NCAR's Community Earth System Model Large Ensemble (CESM-LE) 148 effort [Kay et al., 2015], we develop a new experiment with 29 members for 1990-2025 that 149 explicitly excludes the forcing from Pinatubo (CESM-LE-NoPin) and isolates the externally 150 forced response due to the volcanic eruption. The forced effect due to Pinatubo is quanti-151 fied as the difference between the mean of 29 CESM-LE-NoPin ensemble members and the 152 mean of the 29 CESM-LE members from which these were branched off. This forced ef-153 fect is not directly observable in the real world. Instead, real world observations are akin to a 154 single ensemble member that includes both the forced signal and internal variability [Deser 155 et al., 2012a,b]. As a coupled climate model, each ensemble member of CESM-LE develops 156 its own phasing of internal variability that does not necessarily correspond with the phas-157 ing in the real world observations. The spread across the ensemble indicates the potential 158 magnitude of the Earth system response to Pinatubo across multiple realizations of internal 159 variability. Considering both the forced response and the internal spread, we evaluate the 160 near-term and long-term interior ocean carbon and oxygen effects of Pinatubo, and connect 161 these changes to surface flux patterns. Where appropriate, we place the forced changes and 162 ensemble spread into context with observed changes in the ocean. 163

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2.1 The Community Earth System Model

We use the CESM version 1 [CESM1; Hurrell et al., 2013] to conduct our large en-165 semble simulations. CESM1 consists of atmosphere, ocean, land, and sea ice component 166 models [Danabasoglu et al., 2012; Lawrence et al., 2012; Hunke and Lipscomb, 2008; Hol-167 land et al., 2012]. The coupled atmospheric model is the Community Atmospheric Model 168 version 5 (CAM5), integrated at nominal 1° horizontal resolution with 30 vertical levels 169 [Hurrell et al., 2013]. Volcanic radiative forcing is incorporated in the CESM LE using the 170 forcing dataset of Ammann et al. [2003]. Stratospheric aerosol in CESM1-CAM5 is treated 171 by prescribing a single, zonally averaged species. The prescription consists of a monthly 172 mean mass distributed on a predefined meridional and vertical grid [Neely III et al., 2016]. 173 This aerosol mass is assumed to be comprised of 75% sulfuric acid and 25% water and to 174 have a constant log-normal size distribution. 175

The ocean physical model, Parallel Ocean Program, version 2 [Smith et al., 2010] has 176 nominal 1° horizontal resolution and 60 vertical levels. Mesoscale eddy transport, diapycnal 177 mixing, and mixed layer restratification by submesoscale eddies are parameterized with state-178 of-the-art approaches [Danabasoglu et al., 2020]. The biogeochemical-ecosystem ocean 179 model, known as the Biogeochemical Elemental Cycling (BEC) model, includes multi-nutrient 180 co-limitation on phytoplankton growth and specific phytoplankton functional groups as well 181 as full-depth ocean carbonate system thermodynamics, sea-to-air O_2 and CO_2 fluxes, and a 182 dynamic iron cycle [Moore et al., 2013]. The biogeochemical-ecosystem model compares 183 favorably to observations, though there are some important biases, including weak Southern 184 Ocean CO₂ uptake [Long et al., 2013]. 185

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2.2 CESM No Pinatubo experiment (CESM-LE-NoPin)

The CESM-LE-NoPin setup is identical to the CESM-LE setup, but excludes the ef-187 fect of the eruption by adjusting the volcanic aerosol mass mixing ratio within the model. 188 Specifically, the volcanic aerosol mass mixing ratio values in CESM-LE-NoPin for January 189 1991 to December 1995 were replaced with values from January 1986 to December 1990 190 to simulate a time without impact from volcanic eruptions. Since Pinatubo was the domi-191 nant climatically important volcano during this period, we attribute the resulting climatic 192 and ocean biogeochemical changes to Pinatubo. With this single change in the model setup, 193 we are capturing effects attributable to the physical climate anomalies, however the method-194 ology utilized in this model set up does not consider impacts from volcanic dust deposition 195 on biomass production or other secondary feedbacks on the ocean from volcanic eruptions 196 [Hamme et al., 2010]. 197

Conceptually, the CESM-LE-NoPin ensemble can be thought of as multiple realizations from a "control" climate that did not experience Pinatubo, while the original CESM-LE can be thought of as an "experiment" where each realization, or ensemble member, includes the eruption. We ran the 29 ensemble members of CESM-LE and CESM-LE-NoPin on the same supercomputer (NCAR Cheyenne) to avoid differences in output generated by machine and compiler changes; the original CESM-LE was run on NCAR's Yellowstone machine.

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204 **2.3 Statistical analysis**

205	We present Pinatubo-driven anomalies throughout the manuscript, where anomalies
206	represent the difference between the CESM-LE and the CESM-LE-NoPin output. We quan-
207	tify the forced impact of the eruption as the difference between the CESM-LE and CESM-
208	LE-NoPin ensemble means (X). The internal variability is defined as the standard deviation
209	(σ) across the ensemble members (CESM-LE minus CESM-LE-NoPin) at each time step.
210	Analysis is conducted on monthly model output.

The forced impact of the eruption is statistically significant at the 95% confidence level [*Deser et al.*, 2012a] if its ratio of the ensemble mean difference (X) with the internal spread (σ) is greater than 2 divided by the square root of the degrees of freedom (N-1; here N = 29),

$$\frac{X}{\sigma} \ge \frac{2}{\sqrt{N-1}}.$$
(1)

When considering annual mean anomalies for the years following the eruption (Figures 4-5), we use July as the first month of each year to ensure symmetry around the peak of ENSO. Consistent with previous work on the topic [*Eddebbar et al.*, 2019], we refer to the 12 months following the eruption as Year 0 [July 1991 -June 1992], and subsequent years as Year 1 [July 1992-June 1993], Year 2 [July 1993-June 1994], etc.

219 3 Results

Oxygen and carbon in the ocean are sensitive to a number of different physical processes in the climate system. In this section, we briefly describe the eruption-driven changes in ocean temperature, heat content, mixed layer depth, and circulation that are relevant for oxygen and carbon. We then perform a detailed investigation of the oxygen and carbon anomalies driven by Pinatubo.

225

3.1 Physical response to Pinatubo

The eruption of Pinatubo in June of 1991 drives an immediate reduction in global mean sea surface temperature (SST) followed by a prolonged recovery (Figure 1a). The forced SST anomaly due to Pinatubo reaches a maximum of 0.18°C one year post-eruption, with a statistically significant cooling anomaly persisting for five years post eruption, despite an ensemble spread of ±0.08°C (Figure 1b). Below the sea surface, Pinatubo leads to a sub-

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stantial heat loss, reaching a maximum of -3.5×10^{22} J across the entire water column by 231 mid-1993, with most of this heat loss occurring in the upper 250 meters (Figure 2a,b, 3a). 232 A globally averaged vertical profile Hovmöller plot of the difference of the two ensemble 233 means (CESM-LE minus CESM-LE-NoPin) shows that significant cooling begins in 1992 234 for the upper ocean, with global-mean anomalies as large as 0.2° C penetrating down to 150m 235 (Figure 3a). Smaller, but still significant, anomalies persist to depths below 1000m. Ocean 236 heat content remains significantly altered by the eruption at the 95% confidence level through 237 the year 2000 for the 250 m inventory and persists longer for full depth inventories (Fig-238 ure 2b). Below 1000 m, the Pinatubo effect on heat content remains statistically significant 239 for the duration of our experiments that end in 2024 (-2 x 10²² J, Figure S1), while the upper 240 250 m rebounds toward a heat content statistically indistinguishable from CESM-LE-NoPin 241 after 2004 (Figure 2b). While there is some recovery in the two years following the maxima 242 anomaly in OHC, the recovery stops quite abruptly in 1996 for all depths, and only modest 243 changes are seen in the anomalies after that year, specifically at depths below 250m (Fig-244 ure 2b). Our results show that Pinatubo causes a net heat loss that is not recovered even 3 245 decades after the eruption, consistent with previous modeling work [Frölicher et al., 2011]. 246

Spatial features of sea surface temperature anomalies show that Pinatubo-driven cool-247 ing is concentrated in the tropics in the year immediately following the eruption (Figure 4, 248 left, Year 0). Cooling quickly spreads over much of the surface ocean by Year 1 (1992-93) 249 with significant anomalies, given the spread of internal variability indicated by the model 250 ensemble, throughout much of the Pacific basin (unstippled areas in Figure 4). In Year 1 251 there is also warming surface temperatures in the eastern equatorial Pacific, indicating the 252 development of an El Niño event (Figure S4). In Year 2 (1993-94), this switches to a forced 253 tendency to La Niña patterns in the equatorial Pacific, while northern hemisphere forced re-254 ductions in SST continue. In Year 3 (1994-95), the forced tendency to La Niña is the primary 255 Pinatubo-driven cooling signal that persists. By Year 4 (1995-96), the forced surface cooling 256 has largely dissipated, with internal variability masking any significant signal in the anoma-257 lies. Throughout the first 5 years post eruption (Year 0-4), no statistically significant cool-258 ing is simulated in the Southern Ocean. The Pacific sector of the Southern Ocean shows the 259 strongest forced signal anomalies, although not emerging from the spread of internal vari-260 ability, with warming during Year 0 and 1 followed by a cooling in subsequent years. These 261 spatial maps indicate that the global-mean evolution of temperatures (Figure 3a) is initially 262

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dominated by the Northern extratropics and then by a multi-year tendency to La Niña conditions in the equatorial Pacific.

Significant forced changes in maximum mixed layer depths (maxMLD) are spatially 265 patchy, but do occur in extratropical locations important to upper and deep ocean ventila-266 tion (Figure 4, right). In the North Atlantic subpolar region across Years 0-4, there are some 267 patches of significant forced maxMLD increases, particularly in the eastern gyre and in the 268 Labrador and Irminger Seas. In the North Pacific, mode water regions experience significant 269 forced increase in maxMLD in Year 0 and 1, and some forced decline in Year 4. Only weak 270 forced change in maxMLD anomalies occur in scattered locations throughout the Southern 271 Ocean. 272

273

3.2 Oxygen and carbon response to Pinatubo

The physical changes in temperature and circulation following Pinatubo are accompa-274 nied by pronounced changes in carbon and oxygen distributions and fluxes (Figure 1). The 275 forced oxygen flux anomaly peaks at 42 Tmol yr⁻¹ in 1992, with an ensemble spread (σ) of 276 ± 31.5 Tmol yr⁻¹. The forced carbon flux anomaly reaches 0.29 Pg C yr⁻¹ in 1992, with an 277 ensemble spread ± 0.14 Pg C yr⁻¹. The ensemble mean anomaly in O₂ and CO₂ flux is ro-278 bust at the 95% confidence level with the forced response of these fluxes persisting through 279 1996 (Figure 1d,f). The global mean fluxes are large initially after the eruption due to the 280 cooling of the surface ocean, but then the increased uptake weakens and rebounds to a sig-281 nificant forced reduction in the flux in years 1994-6 as cooling tapers off (Figure 1, left col-282 umn). 283

Oxygen and carbon inventory in the top 1000 m for both ensembles illustrate signifi-284 cant perturbations amid a backdrop of decreasing and increasing long-term trends, respec-285 tively (Figure 2c,e). The oxygen inventory time series reflects the global deoxygenation 286 trend, and a clear divergence between the ensemble means of the CESM-LE and CESM-287 LE-NoPin experiments (Figure 2c). The anomalous oxygen uptake by the oceans immedi-288 ately following the eruption (Figure 1c,d) causes an increase in the O_2 content that is strong 289 enough to temporarily counteract the effects of ocean deoxygenation. This pause in the de-290 oxygenation trend extends though 1995 before the decline resumes (Figure 2c). 291

There are significant Pinatubo-driven oxygen inventory anomalies for both the upper and deep ocean, with positive anomalies (increased oxygen content with the eruption) in the

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upper ocean through 1998 (Figure 2d) and lagged changes for the full depth inventory ex-294 tending for the entire 35 years of this experiment (Figure 2d, Figure S2). Post eruption, oxy-295 gen is immediately absorbed into the upper ocean and then transits to depth quickly where 296 it permanently increases the interior inventory by 60 Tmol (Figure 2d). Globally averaged 297 oxygen concentrations increase by as much as 1 mmol m^{-3} in the upper ocean following 298 the eruption, reaching to depths of 250 m in early 1992 and subsequently spreading through 299 the upper kilometer in 1994-1996 (Figure 3b). Anomalies then become insignificant for the 300 global-averaged upper ocean above 250 m, but anomalies at depths greater than 250 m per-301 sist for the entire length of the simulation (Figure 3b, S3). 302

Pinatubo-driven anomalies in oxygen inventory exhibit large spatiotemporal variabil-303 ity across the ocean (Figure 5, left). The oxygen inventory of the upper 1000 m displays ± 2 304 mol m^{-2} anomalies in the Northern hemisphere and the tropics in Years 1-3; anomalies in 305 the Southern Ocean do not emerge until Years 3-4 and are concentrated in the Pacific sec-306 tor (Figure 5, left). Positive anomalies, indicating greater depth-integrated oxygen due to 307 Pinatubo, emerge first in the western boundary current regions of both the North Pacific 308 and Atlantic basins in Year 1 post eruption, and traverse across the basin with time. In the 309 North Atlantic, subpolar anomalies strengthen from Year 1 to Year 4, concurrent with cool 310 SST anomalies and deeper mixed layer depths in that region (Figure 4). In the North Pa-311 cific, increased oxygen inventory is also linked with cool SST and deeper maxMLD anoma-312 lies (Figure 5, Figure 4). The positive anomalies in the North Pacific have only made it half 313 way across the basin by Year 4, but the positive anomalies continue in that same trajectory 314 in Years 5-9 (not shown). In these extratropical regions, Pinatubo-driven cooling, maxMLD 315 deepening, and increased oxygen inventories are consistent with enhanced ventilation. The 316 small regions exhibiting Pinatubo-driven maxMLD deepening correspond to critically im-317 portant regions for upper ocean oxygenation [van Aken et al., 2011; Deutsch et al., 2006] and 318 drive significant anomalies in the global mean oxygen inventory (Figure 2d, 3b). 319

Anomalous oxygen due to Pinatubo enters the ocean most quickly in the tropical Indian and Pacific, and quickly penetrates into and below the mixed layer in these basins (Figure 6, Figure S7-S8). The largest averaged anomalies are found in the North Pacific basin, exceeding 2 mmol m⁻³ for the regional-average anomaly in the upper ocean by two years post eruption (Figure 6). In all basins, Pinatubo-driven upper ocean oxygen anomalies exhibit seasonality, consistent with intermittent ventilation in wintertime (Figure 6). Anomalies in the North Pacific persist between 100-250m for over a decade. In the North Atlantic,

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winter of Year 1 (1992-1993) experiences a ventilation anomaly that also causes anomalies greater than 2 mmol/m³ between 100 and 250m. For multiple years post eruption, wintertime ventilation in the North Atlantic supplies anomalously high oxygen concentrations into the subsurface thermocline ((Figure 6), Figure S5) where oxygen eventually penetrates to depths below 500m (Figure S8). This signal also emerges through a strengthening of the Atlantic MOC during the late 1990s due to this increase in ventilation (Figure S10).

In contrast to the declining oxygen inventory due to ocean warming, Pinatubo-driven 333 anomalies in air-sea CO2 flux and DIC inventory occur against a background of increasing 334 oceanic CO₂ uptake (Figure 1e) and a steadily increasing DIC inventory (Figure 2e) due 335 to increasing atmospheric CO_2 concentrations prescribed in the modeled atmosphere. The 336 carbon response is associated predominantly with preindustrial carbon, rather than anthro-337 pogenic (not shown); all results presented here are for the total carbon. The 0.29 ± 0.14 Pg 338 C yr⁻¹ increase in ocean uptake of carbon after the eruption (Figure 1e,f) leads to a modest, 339 but statistically significant increase of the ocean DIC inventory of 0.53 Pg C in 1000m inven-340 tory by 1993 (Figure 2f) with anomalies most pronounced in the upper ocean (0.77 Pg C in 341 the upper 250 m, Figure 2f). In contrast to oxygen inventories that increase with the depth of 342 integration (Figure 2d), Pinatubo-driven anomalies in DIC inventory are largest in the upper 343 ocean integrals and decrease with depth. Therefore the anomalies in the shallow depths and 344 full integral become nearly consistent by 1998 (Figure 2f). Figure 3c clearly illustrates that 345 the positive anomalies in global-mean DIC are concentrated in the upper 150 m of the ocean 346 during years 1994-1997 (Figure 3c). The slower equilibration timescale for carbon helps to 347 explain the slower DIC response relative to oxygen. Persistent significant anomalies of DIC 348 due to Pinatubo are not detected at depths below 250 m in the global-mean profile, but there 349 are short-lived forced oscillations between significant positive and negative anomalies of 350 smaller magnitude. 351

Similar to oxygen, we find that Pinatubo-driven DIC anomalies exhibit spatial hetero-352 geneity. For dissolved inorganic carbon inventory, we focus on the upper 250m (Figure 5) 353 where the global mean profiles indicate the largest forced response (Figure 3c). Pinatubo's 354 forced excitement of an El Niño event followed by a La Niña event (Figure S4) is expressed 355 in the upper ocean DIC inventory; the Eastern (Western) Equatorial Pacific exhibits lower 356 (elevated) DIC inventories one year post-eruption, while anomalously high DIC inventories 357 can be found in the Eastern Equatorial Pacific during Years 2-3 post-eruption (Figure 5). In 358 the extratropics, from Years 1-3, particularly in the North, there are also forced increases in 359

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the upper ocean DIC content. This is consistent with increased solubility due to lower annual mean SST in these regions, particularly in Years 1 and 2 (Figure 4, left), that supports increased CO₂ fluxes across the air-sea interface (Figure S6).

The strongest positive forced anomalies in the upper ocean DIC inventory occur in the 363 northern and tropical Pacific and tropical Indian, with some significant increase in the south 364 Pacific as well (Figure 7, Figure S7). In the tropical Pacific, circulation anomalies associ-365 ated with ENSO modify the depth of the thermocline, generating opposite-signed anomalies 366 with depth; the Pinatubo-driven El Niño event leads to decreased DIC in the upper 100 m, 367 while the subsequent La Niña event produces $\sim>3$ mmol m⁻³ increases in upper ocean DIC 368 concentrations (Figure 7). In the tropical Indian, thermocline oscillations also play a role in 369 the inventory anomalies (Figure 7). In the Northern extratropics, upper ocean DIC anoma-370 lies occur several years after the eruption (Figure 7). Unlike oxygen, the additional Pinatubo 371 DIC is concentrated in the upper 100 m and generally does not penetrate to depth (Figure 372 S9). The exception to this is in the tropical Atlantic which shows a positive DIC anomaly 373 reaching down to below 250m by 1998 (Figure S9). Since our division of the regions is made 374 at 30°N, this feature is most likely mode waters that are circulating in the upper subtropical 375 gyre across the 30°N boundary. The positive anomaly persists throughout the length of the 376 simulation at depths between 200 and 400m (Figure S9). In the South Pacific south of 30°S, 377 there are modest positive forced anomalies in DIC above 200m in 1993-1996 (Year 2-4) but 378 the other sectors of the Southern Ocean do not show a similar signal (Figure 7). 379

Despite clear forced signals in the upper ocean inventories of oxygen and carbon, forced 380 signals in air-sea fluxes are difficult to discern with our model ensemble size (Figure S5-381 S6). Even with large signals in some regions, forced signals cannot be identified because 382 of the large magnitude of internal variability in the fluxes (equation 1). Focusing on DJF-383 only fluxes (Figure S5-S6, right) to avoid seasonal cancellation of the signal, does allow for 384 a forced signal to emerge in a few spots (eastern North Atlantic in Year 1 and 3), but on the 385 whole does not allow a forced signal to be identified throughout much of the surface ocean. 386 Inventories are integrated quantities that damp local internal variability, and allow forced sig-387 nals to more clearly emerge (Figure 1-3). 388

Though the flux signals are not statistically identifiable as a forced response at the gridscale, they do indicate a tendency for increased air-sea exchange of oxygen in North Pacific mode waters in Year 0 and 1 and in the North Atlantic subpolar gyre in Year 2-4 (Figure S5).

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DJF anomalies are stronger than annual means in the north, consistent with ventilation being 392 dominantly a wintertime phenomena. For carbon, the strongest annual mean anomalies occur 393 in Year 1 (negative, increased uptake/less efflux with eruption) and in Year 3 and 4 (posi-394 tive, reduced uptake/increase efflux with eruption) in the equatorial Pacific, consistent with 395 ENSO variability (Figure S6). In DJF, there are some patches of significant flux anomalies at 396 subtropical and subpolar latitudes that are mostly negative in Years 0-1 (indicating increased 397 carbon uptake) and then are increasingly positive. These maps support the result that the 398 ocean initially took up more carbon, but then the forced response involved a transition to a 399 state with a reduced sink. 400

401 **4 Discussion**

402

4.1 Physical changes with Pinatubo

Our experiments with the CESM Large Ensemble allow precise separation of the phys-403 ical impacts of Pinatubo and their spatio-temporal evolution in the presence of internal vari-404 ability. Consistent with long-standing knowledge [Church et al., 2005; Gleckler et al., 2006a,b; 405 Stenchikov et al., 2009; Eddebbar et al., 2019; Marshall et al., 2022], we find that Pinatubo's 406 eruption caused widespread global cooling, including spatially distinct reductions in SST, 407 localized increases in maximum mixed layer depths and negative anomalies in upper ocean 408 heat content. The forced surface cooling response, reaching a maximum of 0.18°C, is com-409 parable to observations. NOAA's Optimum Interpolation Sea Surface Temperature (OISST) 410 climate data record shows a global mean SST cooling of 0.12°C with a four year recovery 411 time to return to pre-eruption global mean temperatures [Reynolds et al., 2007]. 412

The eruption of Pinatubo generates ENSO variability in CESM (Figure S4). A forced 413 tendency to El Niño-like conditions emerges about one year after the eruption and is fol-414 lowed by La Niña-like conditions in subsequent years (Figure S4). Over half, or 15 mem-415 bers, of the CESM-LE members develop an El Niño event post-eruption 1992/3 (DJF), and 416 all of those members develop a strong La Niña event in 1994/5 (DJF). In contrast, only 7 of 417 the CESM-LE-NoPin ensemble members develop El Niños in 1992/3, with 6 of them devel-418 oping a La Niña event in 1994/5. The significant ENSO response to the Pinatubo eruption in 419 CESM-LE is consistent with other model experiments and paleoproxies that report the emer-420 gence of El Niño event in the year following a tropical eruption [Brad Adams et al., 2003; 421 Ohba et al., 2013; Maher et al., 2015; Stevenson et al., 2017; Predybaylo et al., 2017; Khodri 422

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et al., 2017; Eddebbar et al., 2019]. In the real world, the Pinatubo eruption occurred dur-423 ing a developing positive El Niño - Southern Oscillation (ENSO) index [NOAA, 2019]. The 424 limitation of the real world is that it is difficult to cleanly discern the eruption-driven climatic 425 signal from the phasing of internal climate variability and the background warming trend 426 [Liu et al., 2018]. The impacts of ENSO preconditioning prior to a large eruption remain an 427 outstanding challenge for the community studying impacts of volcanic eruptions on the cli-428 mate system [Marshall et al., 2022; Swingedouw et al., 2017; Stevenson et al., 2017; Predy-429 baylo et al., 2020; McGregor et al., 2020]. Though the extent and mechanisms driving this 430 El Niño-like response in models are still debated [McGregor et al., 2020], the subsequent La 431 Niña-like response to Pinatubo identified in CESM-LE has received little attention. 432

In contrast to the Pinatubo-driven ENSO response in CESM, the winter (DJF) North 433 Atlantic Oscillation (NAO) index has a significant forced response to the eruption for only 434 about one year during Year 3-4 (1994-1995), while the Southern Annular Mode (SAM) index 435 does not show a significant forced response to the eruption at any time during the model run 436 (Figure S4). This results are consistent with previous modeling studies considering strong 437 volcanic eruptions impact on climate signals which found the tendency for NAO to persist 438 in a positive phase over the first post-eruption decade, beginning in Year 3 post-eruption 439 [Zanchettin et al., 2012]. Likewise for the SAM, McGraw et al. [2016] find that in years fol-440 lowing major volcanic eruptions there is a tendency to a more positive median SAM index, 441 however internal variability is large and ENSO state can impact this connection. 442

Additionally, our results show that Pinatubo forces an increase in the Atlantic Merid-443 ional Overturning Circulation (AMOC) by 1 Sv (4% of the mean), with individual ensem-444 ble members increasing by as much as 5 Sv (20% of the mean) (Figure S10). This is con-445 sistent with previous studies indicating that external forcing from volcanoes has an impact 446 on the overturning circulation [Swingedouw et al., 2017; Fang et al., 2021]. The AMOC 447 strengthening found in these CESM anomalies is larger and occurs earlier than that reported 448 by Zanchettin et al. [2012]. In their last millennium ensemble results they find an AMOC in-449 tensification which culminates roughly one decade after the eruption with anomalies on the 450 order of +0.5 Sv. 451

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4.2 Comparing Pinatubo impacts on carbon and oxygen

Forced carbon and oxygen responses to Pinatubo have quite different spatial patterns (Figure 3,5, S5-S6), but the globally-averaged temporal evolution is reasonably similar. Oxygen is taken up at higher latitudes and deeper horizons than carbon which is primarily taken up at lower latitudes and further up the water column, in agreement with the findings of *Eddebbar et al.* [2019]. Several aspects of the oxygen and carbon systems help to explain these features.

⁴⁵⁹ Oxygen has a much faster air-sea equilibration timescale than carbon, supporting larger ⁴⁶⁰ and more immediate O_2 fluxes following the eruption. In addition, DIC concentrations in-⁴⁶¹ crease downward while oxygen decreases with depth in the ocean; when cooling drives deeper ⁴⁶² mixing it brings up water low in O_2 , but high in CO_2 . Thus, ventilation promotes greater O_2 ⁴⁶³ fluxes, but dampens CO_2 fluxes, hence the larger O_2 uptake than carbon at higher latitudes.

Both carbon and oxygen fluxes experience an immediate forced global increase in ocean uptake and then a few years later, a rebound to a positive anomaly, or less uptake (Figure 1c-f). For both gases, the air-sea gradient, $\Delta pX = pX^{atm} - pX^{ocean}$ (X = O₂ or CO₂), sets the magnitude of the flux. Any anomalous increase in uptake into the surface ocean raises pX^{ocean} and thus reduces the ΔX such that future fluxes will be damped [*Koch et al.*, 2009; *McKinley et al.*, 2020].

Together, these factors help to explain the larger amplitude anomalies in oxygen fluxes and the deeper penetration of oxygen inventory anomalies. When the surface ocean cools and low oxygen waters are delivered to the surface, oxygen can rapidly be exchanged across the air-sea interface and injected into the deep ocean [*Körtzinger et al.*, 2004; *Atamanchuk et al.*, 2020] (Figure 3,6). The window to the surface ocean then closes and the oxygen anomalies are transported at depth (Figure 3).

In contrast, the immediate cooling with Pinatubo primarily increases the carbon carrying capacity by increasing carbon solubility at the surface. Air-sea carbon exchange slowly adds DIC to the ocean and seasonal mixing and mode water formation spreads this anomaly in the upper 150m. In the tropics, fluxes are modulated by the ENSO cycle, leading to reduced outgassing with the initial post-eruption El Niño, and then additional outgassing with the subsequent La Niña event (Figure S6-S7). The accumulation of DIC in the upper ocean in the first years after the eruption is concentrated in the North Pacific, Indian, and Southern Ocean (Figure S7). This accumulation acts to create a back pressure on fluxes in Years 2-3
after the eruption (Figure 1e,f, 5, S6).

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4.3 Pinatubo impact on oxygen fluxes and inventories

Previous model experiments [Frölicher et al., 2009; Eddebbar et al., 2019] suggest 486 a potentially important role for volcanic eruptions in interrupting ocean deoxygenation and 487 modulating the pronounced interannual-to-decadal variability of the observed ocean oxygen 488 content. The global mean oxygen anomalies forced by Pinatubo, which are isolated in our 489 study, are considerable given current trends measured in the world's ocean. Models predict 490 a decline in the global ocean dissolved oxygen inventory of 1-7% by the year 2100 [Keel-491 ing et al., 2010] and estimate that 55 Tmol per year was lost in the 1990s [Schmidtko et al., 492 2017]. Our model results indicate that the eruption of Pinatubo led to maximum increase in 493 interior oxygen of about 100 Tmol in the top 1000m over the 4 years following the eruption 494 (Figure 2, 3), more than offsetting the expected deoxygenation for the first half of 1990s and 495 leading to a net increase in the oxygen inventory of about 60 Tmol by the end of the simula-496 tion. 497

Another interesting feature of our results is that oxygen anomalies are decoupled in 498 depth from temperature changes in CESM, suggesting processes such as changes in trans-499 port or biogeochemical rates as drivers of oxygen uptake in addition to the solubility effects, 500 as previously suggested by [Eddebbar et al., 2019]. For example, temperature anomalies 501 are pronounced in upper 0-100 m, while O2 anomalies are intensified in the 50-200 m depth 502 range (Figure 3). Oxygen changes are also generally more pronounced at depth below 250m 503 (Figure 2d, Figure S8), which may offer new insights on the response of ocean circulation to 504 volcanic eruptions. The intensification of the AMOC (Figure S10) suggests an increase in 505 the advective supply of oxygen to depth as a result of volcanic eruption in the Atlantic basin. 506 Pronounced cooling and a deepened mixed layer at mid and high latitudes likely lead to in-507 tensified oxygen uptake and subduction of newly ventilated waters to depth. 508

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4.4 Mechanisms of air-sea CO₂ flux anomalies with Pinatubo

McKinley et al. [2020] used a simple box model forced with atmospheric pCO₂ and global-mean upper ocean heat content anomalies associated with tropical volcanos to propose a mechanistic explanation for globally integrated air-sea CO₂ flux anomalies since the ⁵¹³ 1980s. The box model closely replicates (r>0.9) the signals found in ensembles of ocean ⁵¹⁴ hindcast models and observation-based pCO₂ products. Based on this evidence, *McKinley* ⁵¹⁵ *et al.* [2020] were the first to propose a significant role for external forcing from Pinatubo in ⁵¹⁶ the variability of the ocean carbon sink in the 1990s.

Here, with CESM-LE, we find a significant forced anomaly of 0.29 Pg C yr⁻¹ in the 517 1992 globally-integrated air-sea CO₂ flux forced by Pinatubo in CESM-LE; and individ-518 ual members of the ensemble have flux anomalies greater than 0.5 Pg C yr^{-1} (Figure 1e,f). 519 CESM-LE also reveals significant spatial structure in the carbon flux and DIC inventory 520 response to the eruption of Pinatubo-the ocean's carbon response to Pinatubo is far from 521 globally uniform (Figure 5,7, S6). In the subtropics and the northern high latitudes, the up-522 per ocean absorbs more carbon, particularly in the subtropics, while ENSO dominates the 523 tropical response (Figure 5, 7). This heterogeneous spatial response is not at all captured in 524 the box model, yet the box model's CO_2 flux anomaly of 0.5 Pg C yr⁻¹ is within a factor of 525 two of the CESM-LE forced response. CESM-LE also indicates a similar forced reduction 526 in the ocean carbon sink in 1994-1995 as in the box model. This feature is consistent with 527 more DIC being held in the upper ocean (Figure 5) where it can raise surface ocean pCO_2 528 and damp the flux (Figure S6) [McKinley et al., 2020]. 529

The evolution of the global-mean ocean heat content (OHC) and global-mean DIC 530 profile (Figure 3) demonstrates the global-mean relationship between upper ocean cooling 531 and DIC content that the box model successfully mimics. The forced change in OHC due to 532 Pinatubo $(-3.5 \times 10^{22} \text{ J})$ is within the range estimated from observations and other modeling 533 studies [Church et al., 2005; Gleckler et al., 2006a, 2016; Stenchikov et al., 2009; Eddebbar 534 et al., 2019; DeVries, 2022]. The OHC anomaly in the 200 m deep box model of McKinley 535 et al. [2020] is within a factor of two (-5.5×10^{22} J). As in the box model, the globally aver-536 aged behavior of CESM-LE is for the negative OHC anomalies to enhance solubility and 537 allow for enhanced air-sea fluxes to persist for long enough (several years) such that addi-538 tional carbon can be absorbed in the upper ocean (Figure 3). These CESM-LE experiments 539 demonstrate both this global-mean forced response and allow for deeper understanding of the 540 spatially variable mechanisms forced by Pinatubo. 541

Another study looking at the external forcing of the Pinatubo eruption on the climate system found a cooling of upper ocean (0-300m) ocean heat content and a subsequent recovery to near zero OHC anomaly by 1996 [*DeVries*, 2022]. However, the models used by

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DeVries [2022] utilize only historical SST to represent Pinatubo's external forcing in a steady 545 circulation ocean model. Since these SST anomalies impacted only the top model layer of 10 546 m depth, the resulting globally-integrated OHC anomaly with Pinatubo (-1x10²² J) was sub-547 stantially smaller than most observational studies [Church et al., 2005; DeVries, 2022] and 548 more than 3 times smaller than the forced response estimated here with CESM-LE. There-549 fore their resulting small externally forced air-sea CO₂ flux response is consistent with the 550 underestimation of globally-integrated upper ocean cooling and the lack of ENSO response 551 or ventilation changes in a model with steady circulation. 552

CESM-LE demonstrates a clear CO₂ flux anomaly due to Pinatubo in the global in-553 tegral (Figure 1e,f). But at the local scale, air-sea flux anomalies rarely have a statistically 554 significant forced response (Figure S6). This is because the large internal variability in sur-555 face fluxes obscures the forced signal. This finding is directly comparable to the finding that 556 the air-sea CO₂ flux response to COVID-19 emissions reductions is not detectable at the lo-557 cal scale [Lovenduski et al., 2021]. Large internal variability presents a particular challenge 558 to the potential for local flux observations to directly identify climatic signals and argues for 559 continued integration of data into observation-based products from which large-scale signals 560 can be identified [Fay and McKinley, 2021; Fay et al., 2021]. 561

CESM-LE indicates that the regional centers for CO₂ flux anomalies due to Pinatubo 562 are primarily in the Northern hemisphere and the tropics, but not in the Southern Ocean (Fig-563 ure S6). This contrasts to observation-based products that suggest large amplitude decadal 564 variability in Southern Ocean CO₂ fluxes [Landschützer et al., 2015; Hauck et al., 2020; 565 Bennington et al., 2012]. Other mechanisms may be responsible for observed large ampli-566 tude Southern Ocean decadal variability [Gruber et al., 2019]. Alternatively, in-situ sam-567 pling [Bakker et al., 2016] in the Southern Ocean may have been too sparse to allow for ac-568 curate reconstructions [Gloege et al., 2021]. With respect to global mechanisms, CESM-LE 569 indicates that the more vigorous overturning of the 1990s, identified by *DeVries et al.* [2017] 570 as a potential mechanism for ocean carbon sink variability, may have been externally forced 571 by Pinatubo. Better quantifying the magnitude and mechanisms of CO₂ flux decadal vari-572 ability globally and in the Southern Ocean is an important focal point for current ocean car-573 bon research. 574

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575 **4.5 Future Work**

With this analysis, we have only just begun to explore all the insights available regarding the impact of the Pinatubo eruption on the ocean and its biogeochemistry. There is much more to be done in terms of understanding the full extent of Pinatubo's impact on ocean physics and biogeochemistry at global, regional, and local scales.

Integrated column inventories and globally integrated fluxes clearly demonstrate the impact of Pinatubo on ocean oxygen and carbon, but locally, significant forced changes in air-sea fluxes are difficult to identify (Figure S6). Because of the magnitude of internal variability at the surface, future work could expand the number of ensemble members to pinpoint forced changes in surface fluxes.

We highlight here that the Pinatubo effects on ocean biogeochemistry explored in this 585 modeling experiment include the climate impacts of volcanic aerosols on ocean biogeochem-586 istry but do not simulate direct biogeochemical changes associated with increased micronu-587 trient deposition from volcanic ash. Observational studies of smaller eruptions suggest vol-588 canic ash deposition may significantly influence carbon cycling through fertilizing plankton 589 growth at regional scales [Hamme et al., 2010; Langman et al., 2010]. The direct biogeo-590 chemical contribution of atmospheric deposition of micronutrients by volcanic ash may have 591 additional and complex effects on carbon and oxygen distributions and inventories. These 592 effects are outside the scope of this work, but are worth examining in follow on experiments. 593

CESM is just one of many Earth system models that have previously generated large ensembles [*Deser et al.*, 2020]. All models are imperfect representations of the real Earth for example, this version of CESM underestimates Southern Ocean CO₂ uptake [*Long et al.*, 2013] and we do not know if this bias has a role in the small Southern Ocean impacts from Pinatubo that we find here. It would be of great value to have other modeling centers conduct large ensembles without Pinatubo so that different estimates of forced responses and representation of volcanic aerosol forcings could be compared.

We are currently using the CESM ensembles to investigate the impact of the Pinatubo eruption on hydrographic observations of ocean biogeochemistry [*Olivarez, H.C., Lovenduski, N.S., Eddebbar, Y.A., Fay, A.R., Levy, M., Long, M.C., and McKinley, G.A., The Impact of the Pinatubo Climate Perturbation on Global Ocean Carbon and Biogeochemistry, in preparation for Global Biogeochemical Cycles*]. The bulk of ocean biogeochemical observations that anchor long-term trends were collected in the years following the Pinatubo

eruption through the World Ocean Circulation Experiment / Joint Global Ocean Flux Study

608 (WOCE / JGOFS) [*Boyer*, 2018].

609 Comprehensive model output is available for scientists to investigate other components 610 of the Earth system, such as the atmosphere, sea ice and cryosphere.

5 Conclusions

With two initial-condition large ensembles, we have isolated the impacts of the 1991 eruption of Mt. Pinatubo on ocean physical and biogeochemical properties. Pinatubo forced the ocean to cool to a peak of 0.18° C at the surface and to lose 3.5×10^{22} J of heat. Pinatubo forced an El Niñõ event one year after the eruption, and then La Niñã for the two subsequent years. Upper ocean ventilation increased in key regions, allowing for the penetration of oxygen anomalies to depth. These simulations indicate that the long-term effect of Pinatubo on the ocean heat budget was a loss of 2×10^{22} J that persists for multiple decade.

Associated with these physical changes, the ocean absorbed oxygen and carbon, with 619 peak globally integrated forced flux anomalies in 1992 of 42 Tmol O₂ yr⁻¹ and 0.29 Pg C 620 yr⁻¹, respectively. In the tropics and northern high latitudes, the eruption's impact on oxygen 621 is dominated by surface cooling and subsequent ventilation to mid-depths, while the carbon 622 anomaly is associated with solubility changes and eruption-generated ENSO variability. In-623 creased inventories of both gases are found mostly in the tropics and Northern hemisphere, 624 but are very limited in the Southern Ocean. Oxygen anomalies penetrate to the deep ocean, 625 while carbon anomalies remain concentrated in the upper 150 m. For both, full-depth inven-626 tories are permanently altered. 627

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- ous work done by the CESM Large Ensemble Community Project.
- 637 Open Research: The CESM source code is freely available at http://www2.cesm.ucar.edu.
- ⁶³⁸ The model outputs described in this paper can be accessed at www.earthsystemgrid.org.

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Figure 1. Left column: CESM-LE (blue) and CESM-LE-NoPin (red) individual members (thin lines) and ensemble mean (thick line) time series for global mean SST (top, degC), Oxygen flux (middle, Tmol/yr), and CO₂ Flux (bottom, Pg/yr) for 1990-2004. Right column: CESM-LE minus CESM-LE-NoPin difference for each variable with thicker line indicating significant difference between the two ensembles at 2σ [*Deser et al.*, 2012a]. Time series are seasonally detrended and smoothed with a 12-month running mean. Gray triangles mark timing of eruption. Full time series through 2025 available in Figure S1. -32-



Figure 2. Left column: CESM-LE (blue) and CESM-LE-NoPin (red) individual members (thin lines) 944 and ensemble mean (thick line) time series for global mean Ocean Heat Content (top, Joules 10²²), Oxygen 945 inventory (middle, Pmol), and Dissolved Inorganic Carbon inventory (bottom, Pg) for top 1000m. Inset on 946 DIC inventory (bottom, left) shows a zoomed in ensemble mean time series for 1992-1995 to highlight the 947 difference post eruption. Right column: CESM-LE minus CESM-LE-NoPin inventory difference for each 948 variable with thicker line indicating significant difference between two ensembles at 2σ [Deser et al., 2012a]. -33-949 Inventory plots include lines for depths 250m, 500m, 1000m and full depth. Time series are seasonally de-950 trended, smoothed with a 12-month running mean. Gray triangle marks timing of eruption. Full time series 951 through 2025 available in Figure S2. 952



Figure 3. Globally averaged vertical profile of difference plots (CESM-LE minus CESM-LE-NoPin) for ensemble mean in a) temperature (°C) b) $[O_2]$ (mmol/m³), and c) [DIC] (mmol/mm³). Stippling indicates time/depth where differences are not significant at the 95% confidence level [*Deser et al.*, 2012a]. Positive anomalies (warm colors) indicate greater values with the eruption of Pinatubo while negative anomalies (cool colors) indicate lower values with the eruption. Full model time period available in Figure S3.



Figure 4. Evolution of annual mean anomalies (CESM-LE minus CESM-LE-NoPin) sea surface temperature (SST) and maximum mixed layer depth (maxMLD) during the first five years following the June 1991 eruption of Pinatubo: Year 0 (July 1991-June 1992), Year 1 (July 1992-June 1993); Year 2 (July 1993-June 1994); Year 3 (July 1994-June 1995); Year 4 (July 1995-June 1996). SST anomalies are calculated by removing the seasonal cycle and annually averaging over respective months. Positive anomalies (warm colors) indicate warmer temperatures and deeper maximum mixed layer depths with the eruption of Pinatubo. Stippling indicates areas without significant difference between the two ensembles at 2σ [*Deser et al.*, 2012a].



Figure 5. Evolution of annual mean anomalies (CESM-LE minus CESM-LE-NoPin) depth integrated O_2 (top 1000m) and DIC (top 250m) concentrations during the first five years following the June 1991 eruption of Pinatubo: Year 0 (July 1991-June 1992), Year 1 (July 1992-June 1993); Year 2 (July 1993-June 1994); Year 3 (July 1994-June 1995); Year 4 (July 1995-June 1996). Anomalies are calculated by removing the seasonal cycle and annually averaging over respective months. Positive anomalies (warm colors) indicate greater depth-integrated O_2 or DIC with the eruption of Pinatubo. Stippling indicates areas without significant -36-

difference between the two ensembles at 2σ [Deser et al., 2012a].



Figure 6. Regionally averaged vertical profile of difference (CESM-LE minus CESM-LE-NoPin) plots for ensemble mean O_2 inventory (mmol/m³). Separations are made for the Pacific, Atlantic, and Indian basins into northern (>30°N), tropical (30°N-30°S), and southern sections (<30°S) while the global profile is shown in the top right panel. Stippling indicates time/depth where differences are not significant at the 95% confidence level [*Deser et al.*, 2012a]. Positive anomalies (warm colors) indicate greater oxygen inventory values with the eruption of Pinatubo while negative anomalies (cool colors) indicate lower oxygen with the eruption. Similar plot with depth extending to 1000m is available in Figure S8.



Figure 7. Regionally averaged vertical profile of difference (CESM-LE minus CESM-LE-NoPin) plots for ensemble mean DIC inventory (mmol/m³). Separations are made for the Pacific, Atlantic, and Indian basins into northern (>30°N), tropical (30°N-30°S), and southern sections (<30°S) while the global profile is shown in the top right panel. Stippling indicates time/depth where differences are not significant at the 95% confidence level [*Deser et al.*, 2012a]. Positive anomalies (warm colors) indicate greater DIC inventory values with the eruption of Pinatubo while negative anomalies (cool colors) indicate lower DIC levels with the eruption. Similar plot with depth extending to 1000m is available in Figure S9.

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Supporting Information for "Immediate and long-lasting impacts of the Mt. Pinatubo eruption on ocean oxygen and carbon inventories"

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1. Figures S1 to S11

Introduction This supporting information provides additional figures to support the findings presented in the manuscript. We show the complete time series (1990-2025) for most of the main figures as well as additional information related to climate indices which help with the interpretation of the results.

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Figure S1. Left column: CESM-LE (blue) and CESM-LE-NoPin (red) individual members (thin lines) and ensemble mean (thick line) time series for global mean SST (black, degC), Oxygen flux (teal, Tmol/yr), and CO₂ Flux (magenta, Pg/yr) for full model time series (1990-2025). Right column: CESM-LE minus CESM-LE-NoPin difference for each variable with thicker line indicating significant difference between two ensembles at 2σ Deser:2012a. Time series are seasonally detrended, smoothed with a 12-month running mean. Gray triangle marks timing of eruption.



Figure S2. Left column: CESM-LE (blue) and CESM-LE-NoPin (red) individual members (thin lines) and ensemble mean (thick line) time series for global mean Ocean Heat Content (blue, Joules 10^{22}), Oxygen inventory (orange, Pmol), and Dissolved Inorganic Carbon inventory (green, Pg) for top 1000m for full model time series (1990-2025). Right column: CESM-LE minus CESM-LE-NoPin inventory difference for each variable with thicker line indicating significant difference between two ensembles at 2σ Deser:2012a. Inventory plots include lines for depths 250m, 500m, 1000m and full depth. Time series are seasonally detrended, smoothed with a 12-month running mean. Gray triangle marks timing of eruption. June 30, 2022, 3:52pm



Figure S3. Globally averaged vertical profile of difference plots (CESM-LE minus CESM-LE-NoPin) for ensemble mean in a) temperature (°C) b) $[O_2] \pmod{m^3}$, and c) [DIC] (mmol/mm³) for full model time period (1990-2025). Stippling indicates time/depth where differences are not significant at the 95% confidence level Deser:2012a. Positive anomalies (warm colors) indicate greater values with the eruption of Pinatubo while negative anomalies (cool colors) indicate lower values with the eruption.



Figure S4. CESM-LE (blue) and CESM-LE-NoPin (red) individual members (thin lines) and ensemble mean (thick line) time series of pertinent climate indices: (a) monthly mean Niño 3.4 index (b) Southern Annual Mode (SAM), and (c) winter (DJF) North Atlantic Oscillation (NAO). Thicker line segments on ensemble means indicate significant difference between two ensembles at 2σ Deser:2012a. June 30, 2022, 3:52pm



Figure S5. Evolution of annual mean anomalies (CESM-LE minus CESM-LE-NoPin) of oxygen fluxes during the first five years following the June 1991 eruption of Pinatubo: Year 0 (July 1991-June 1992), Year 1 (July 1992-June 1993); Year 2 (July 1993-June 1994); Year 3 (July 1994-June 1995); Year 4 (July 1995-June 1996). Anomalies are calculated by removing the seasonal cycle and annually averaging over respective months. Positive flux anomalies (warm colors) indicate increased efflux of O_2 in ocean efflux regions or less uptake with the eruption of Pinatubo. Negative flux anomalies (cool colors) indicate less efflux or increased uptake with the eruption of Pinatubo. Stippling indicates areas without significant difference between the two



Figure S6. Evolution of annual mean anomalies (CESM-LE minus CESM-LE-NoPin) of carbon fluxes during the first five years following the June 1991 eruption of Pinatubo: Year 0 (July 1991-June 1992), Year 1 (July 1992-June 1993); Year 2 (July 1993-June 1994); Year 3 (July 1994-June 1995); Year 4 (July 1995-June 1996). Anomalies are calculated by removing the seasonal cycle and annually averaging over respective months. Positive flux anomalies (warm colors) indicate increased efflux of CO_2 in ocean efflux regions (e.g. equatorial Pacific) or less uptake with the eruption of Pinatubo. Negative flux anomalies (cool colors) indicate less efflux or increased uptake with the originatubo. Stippling indicates areas without significant



Figure S7. Regional contributions to O_2 (left) and DIC (right) 1000m concentrations anomalies (CESM-LE minus CESM-LE-NoPin). Ensemble mean time series, with 12-month running mean, for the North Pacific and Atlantic ($\gtrsim 30^{\circ}$ N), Tropical Pacific and Atlantic (30° N - 30° S), Indian Ocean, and Southern Ocean. Can be compared to global values in Figure 2b.



Figure S8. Regionally averaged vertical profile of difference (CESM-LE minus CESM-LE-NoPin) plots for ensemble mean O_2 inventory (mmol/m³) for full model time period (1990-2025). Separations are made for the Pacific, Atlantic, and Indian basins into northern ($\gtrsim 30^{\circ}$ N), tropical (30° N- 30° S), and southern sections ($i30^{\circ}$ S). Stippling indicates time/depth where differences are not significant at the 95% confidence level Deser:2012a. Positive anomalies (warm colors) indicate greater oxygen inventory values with the eruption of Pinatubo while negative anomalies (cool colors) indicate lower oxygen with the eruption.



Figure S9. Regionally averaged vertical profile of difference (CESM-LE minus CESM-LE-NoPin) plots for ensemble mean DIC inventory (mmol/m³) for full model time period (1990-2025). Separations are made for the Pacific, Atlantic, and Indian basins into northern ($i30^{\circ}$ N), tropical (30° N- 30° S), and southern sections ($i30^{\circ}$ S). Stippling indicates time/depth where differences are not significant at the 95% confidence level Deser:2012a. Positive anomalies (warm colors) indicate greater DIC inventory values with the eruption of Pinatubo while negative anomalies (cool colors) indicate lower DIC levels with the eruption.





Figure S10. Time-mean Atlantic Meridional Overturning Circulation (AMOC) from (a) the "control" CESM-LE-NoPin ensemble mean (yrs 1995-99 mean) and (b) CESM-LE minus CESM-LE-NoPin ensemble mean anomaly (yrs 1995-99 mean). The contour interval in (a) is 5 Sv. Stippling on (b) indicates depth/latitude where ensemble mean differences are not significant at the 95% confidence level Deser:2012a. Positive anomalies (warm colors) indicate stronger AMOC values with the eruption of Pinatubo while negative anomalies (cool colors) indicate weaker AMOC values with the eruption. (c) shows a time series of the maximum AMOC at 45°N in CESM-LE (blue) and CESM-LE-NoPin (red) individual members (thin lines) and ensemble mean (thick lines). CESM-LE minus CESM-LE-NoPin anomalies (d) for the ensemble mean (thick line) along with individual ensembles representing the three largest (dark green thin lines) and three smallest (light green thin lines) changes for the time period. Thicker line segments on ensemble means (d) indicate significant difference between two ensembles at 2σ Deser:2012a.



Figure S11. Mean state maps of 1990s CESM-LE-NoPin ensemble mean for (a) SST (contour interval 5°), (b) maximum MLD (contour interval 100m) (c) 1000m O₂ inventory (contour interval 25 mol/m²), (d) 250m DIC inventory (contour interval 10 mol/m²), (e) O₂ flux (contour interval 2 mol/m²/yr), (f) CO₂ flux (contour interval 1 mol/m²/yr), (g) DJF O₂ flux (contour interval 10 mol/m²/yr), (h) DJF CO₂ flux (contour interval 2 mol/m²/yr).