Title: Acceleration of recent oxygen decline in the tropical Pacific by aerosol pollutants

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First paragraph: Dissolved oxygen in the mid-depth tropical Pacific Ocean has declined in the last several decades¹. The resulting expansion of the oxygen minimum zone has consequences for the region’s ecosystem² and biogeochemical cycles³, but the causes of the oxygen decline are not yet fully understood. Here we combine models of atmospheric chemistry and ocean circulation and biogeochemical cycling to test the hypothesis that atmospheric pollution over the Pacific Ocean contributed to the redistribution of oxygen in deeper waters. We simulate the
pollution-induced enhancement of atmospheric soluble iron and fixed nitrogen deposition and its impacts on ocean productivity and biogeochemical cycling for the late 20th century. The model reproduces the magnitude and large-scale pattern of the observed oxygen changes from the 1970s to the 1990s, and the sensitivity experiments reveal the reinforcing effects of pollution-enhanced iron deposition and natural climate variability. Despite the aerosol deposition being the largest in mid-latitudes, its effect on oceanic oxygen is most pronounced in the tropics, where ocean circulation transports added iron to the tropics leading to an increased regional productivity, respiration, and subsurface oxygen depletion. These results suggest that anthropogenic pollution can interact and amplify climate-driven impacts on ocean biogeochemistry, even in remote ocean biomes.

Main Text:

The tropical Pacific Ocean contains a High-Nutrient-Low-Chlorophyll (HNLC) region, where a scarcity of the micronutrient iron limits biological productivity. Below the surface HNLC region (Fig 1A) lay some of the most voluminous oxygen minimum zones (OMZs) of the world oceans. Understanding the mechanisms creating these OMZs and its variability is important as benthic and pelagic organisms are sensitive to oxygen concentrations ([O2])6. In addition, denitrification under suboxic conditions ([O2]<5 μmol L-1) accounts for approximately half the loss of the bioavailable nitrogen in the oceans which impacts the oceanic inventory of nitrate and produces the potent greenhouse gas nitrous oxide. Observed [O2] in the tropical Pacific OMZ has shown a prominent decline in recent decades (Fig 1B). The solubility of gases in seawater decrease with increasing temperature, but the recent decline of tropical Pacific [O2] was not accompanied by a temperature increase, indicating that the cause of the recent oxygen
decline in this region must include changes in biological oxygen consumption and/or ocean circulation. Recent studies proposed that the dominant mode of the North Pacific climate variability, the Pacific Decadal Oscillation (PDO), and associated increase in the tropical upwelling and productivity since the 1980s may have contributed to the expansion of the tropical Pacific OMZ. However, the excess nitrate in the surface of this region permits an additional mechanism for the increasing productivity, if the iron supply were to increase.

Major sources of iron to the open ocean include aerosol deposition, continental shelf sediments and hydrothermal vents. Among these sources, iron delivered through aerosol deposition is highly variable and has undergone major anthropogenic perturbations due to the emission of atmospheric pollutants as well as variations in dust emissions, with potential impacts on marine biogeochemistry. The scavenging of atmospheric pollutants (i.e., inorganic and organic acids) by dust particles can solubilize mineral iron during its atmospheric transport, significantly increasing the bioavailable fraction of dust iron upon deposition to the surface ocean. Anthropogenic fuel combustion is also a significant regional source of soluble iron. Atmospheric pollution has increased the input of fixed nitrogen to the surface oceans, which can moderate the nitrogen limitation of phytoplankton. We examine whether increased delivery of micro and macronutrients to the North Pacific Ocean enhanced biological productivity and subsurface respiration, contributing to the recent decline of $[O_2]$ in the tropical Pacific.
To evaluate the possible connections between atmospheric pollution, ocean productivity and the OMZ, we perform computational simulations of atmospheric chemistry and its impact on marine biogeochemistry. Fluxes of the aerosol soluble iron (sol-Fe) and fixed nitrogen are calculated using the three-dimensional atmospheric chemical transport model GEOS-Chem coupled with a comprehensive dust-iron dissolution scheme\textsuperscript{15}. The resulting aerosol nutrient deposition fields are then used to drive an ocean biogeochemistry model (MITgcm) in an offline mode using data-constrained circulation fields\textsuperscript{19}. The model includes a representation of iron and macronutrient co-limitation of biological productivity. Detailed model description is provided in the Method section. The model is first spun up using a climatological ocean circulation and preindustrial aerosol deposition fields. The increase of anthropogenic pollution from the 1750 and 2002 is estimated based on the global coal production time series\textsuperscript{20} while the dust emission is held constant. In order to capture the full effect of anthropogenic pollution, hindcast simulations are performed from 1750 to 2002, and the last 50 years of the simulation (1952-2002) includes ocean circulation variability to evaluate the combined effects of aerosol pollutants and natural climate variability.

The atmospheric processing of dust in the contemporary condition\textsuperscript{15} has substantial impacts on the solubility of dust iron and its rate of deposition at the sea surface, relative to the preindustrial state (Fig 2A). A large increase in sol-Fe deposition occurred in the North Pacific Ocean to the east of Asia, while it is largely unaffected over the equatorial Pacific Ocean. Averaging over the central North Pacific (150°E-120°W, 0°-40°N), the soluble fraction of aerosol iron increased from 0.61% to 1.80%, tripling the annual mean sol-Fe flux from 5.2 to 14.8μgFe m\textsuperscript{-2} month\textsuperscript{-1} between preindustrial and contemporary states, consistent with earlier studies\textsuperscript{21,22}. Nitrogen deposition exhibit similar spatial patterns to sol-Fe in the Pacific Ocean.
(Fig 2B). Averaging over the central North Pacific Ocean, the annual mean fixed nitrogen flux increased by approximately 70%, from 0.32 to 0.55 mmolN m\(^{-2}\) month\(^{-1}\), also consistent with earlier studies\(^{22}\).

\[\text{Figure 2 about here}\]

The combination of climate variability and the long-term increase in macro and micronutrient deposition alters the large-scale patterns of modeled productivity and subsurface \([O_2]\) (Fig 3). While changes in export production cannot be evaluated from historical observations, the associated changes in \([O_2]\) can be evaluated against the instrumental record. Model-simulated changes of \([O_2]\) in the thermocline between the 1970s and 1990s (Fig 3A) are in good agreement with the historic observations, in magnitude and spatial pattern (Fig 1B). The average \([O_2]\) in the tropical Pacific thermocline (10\(^{\circ}\)S to 10\(^{\circ}\)N, 150\(^{\circ}\)E to 80\(^{\circ}\)W, 260 to 710m depth) decreased by 5.1 \(\mu\text{mol L}^{-1}\) from 1970s to 1990s in the model, slightly underestimating the observed decline of 5.9 \(\mu\text{mol L}^{-1}\) in the same region (Fig 1B). The strongest \([O_2]\) decline occurs in the eastern tropical Pacific, and it increases in the western subtropical thermocline. These features are consistent with previous studies of historic observations\(^{9,23}\).

\[\text{Figure 3 about here}\]

The tropical \([O_2]\) decline coincides with the increased export of organic matter (Fig 3B), indicating that the increased biological productivity contributed to the \([O_2]\) decline there.
The model simulation includes three factors to explain observed changes in \([O_2]\): (i) the variability of ocean circulation, (ii) the pollution-enhanced sol-Fe deposition and (iii) the pollution-enhanced fixed nitrogen deposition. The circulation variability can alter positions of the water masses and the transport of dissolved oxygen. It can also perturb the supply of nutrients to the surface and alter biological productivity. The pollution-enhanced sol-Fe and fixed nitrogen fluxes can stimulate ocean productivity and subsurface respiration. To separate these effects (i.e., ocean circulation from nutrient deposition) we perform attribution experiments in which each mechanism is eliminated one at a time. By taking the difference between the full simulation and each of the sensitivity runs, we estimate the effects of individual mechanisms. To suppress the effect of ocean circulation variability, a sensitivity run was performed using the climatological ocean circulation. To suppress the effect of sol-Fe and fixed nitrogen deposition, two sensitivity runs are performed with the preindustrial sol-Fe and fixed nitrogen deposition fields respectively.

The effects of circulation variability (Fig 4A) and the pollution-enhanced sol-Fe deposition (Fig 4C) are significantly greater than that of fixed nitrogen deposition (Fig 4E), consistent with a recent study using a more sophisticated marine ecosystem model\(^\text{22}\). Table S1 lists the contributions of each mechanism to the changes in sinking organic flux and \([O_2]\) from 1970s to 1990s in the tropical Pacific. The combined effects are smaller than the sum of the individual effect, reflecting the nonlinearity of the system. Basin-scale changes in sinking organic matter (Fig 4BDF) generally have opposite signs from that of oxygen since the respiratory oxygen loss is driven by the decomposition of the sinking organic matter. At subpolar latitudes, the circulation-driven variability exhibits a strong east-west gradient in oxygen but not
in sinking organic flux, reflecting the dominant role of shifts in water masses and variability of
thermocline ventilation rates\textsuperscript{24}.

Despite a monotonic increase in atmospheric deposition of sol-Fe in the mid-latitude
North Pacific, the sinking organic flux actually declines from 1970-1990 in the western
subtropics between 20°N-30°N (Fig 4D), causing an increase in thermocline [O\textsubscript{2}] there (Fig 4C).
The effect of enhanced sol-Fe deposition initially increases the ocean productivity across all
latitudes. However, the surface macronutrient supply to the subtropics eventually decreases due
to the increasing utilization of those nutrients in upstream regions associated with the iron
fertilization.

The pattern of marine productivity and subsurface [O\textsubscript{2}] changes are markedly different
from that of the changes in aerosol deposition to the sea surface. Both sol-Fe and fixed nitrogen
deposition increased most strongly in the mid-latitudes and did not significantly increase in the
equatorial Pacific (Fig 2), yet the pollution-induced changes in ocean productivity and [O\textsubscript{2}] are
largest in the tropics (Fig 4). This implies that the ocean currents transport the iron from the
source regions in the mid-latitudes through the interior ocean to the tropical upwelling regions.
In our simulations, organic ligand concentration is set to a uniform constant at 1nM, greater than
the typically observed iron concentrations in the mid-depth Pacific (Fig S1). The excess ligand
moderates the scavenging loss of iron, allowing the long-range transport\textsuperscript{25}. The distribution of
pollution-induced increase in the dissolved iron indicate that it spreads along the density surfaces
of the North Pacific gyre circulation (Fig S3) that are ventilated from the region of increased sol-
Fe deposition. Modeled near-surface dissolved iron is strongly depleted relative to observations, potentially indicating an overestimation of sensitivity to sol-Fe deposition.

While the atmospheric chemical transport model captures the observed pattern of sol-Fe deposition, its historical rate of increase and the interannual variability of dust emissions are uncertain. We evaluate the sensitivity of our results using additional simulations in which the trend of sol-Fe deposition is reduced (x0.25 and x0.5) or increased (x2 and x4) relative to the standard simulation (Fig S4). The simulated oxygen decline from 1970s to 1990s varies by about 15% from 4.5 to 5.2 μmol L⁻¹ over the tropical Pacific thermocline among the sensitivity runs (Table S2), indicating the overall robustness of our conclusion. While different emission scenarios and meteorological fields may lead to modest shifts in the iron and nitrogen deposition fields and the OMZ development, the essential features described in this paper is likely robust considering the strong increase in the sol-Fe deposition and the reinforcing, but modest increase of nitrogen deposition. A more realistic situation may include the additional processes and feedbacks involving nitrogen cycling and marine ecosystem. An increase in fixed nitrogen supply may weaken the nitrogen fixation by diazotroph, compensating the anthropogenic nitrogen input. Increased sol-Fe deposition may potentially alter the regional rates of nitrogen fixation. The expansion of the OMZ may also promote the loss of fixed nitrogen via denitrification. Furthermore, continuous increase in sol-Fe and fixed nitrogen deposition may eventually lead to the phosphorus limitation. Our simulations do not include these potentially important feedbacks.

The combined effects of the anthropogenic pollution with the interannual and decadal climate variations likely caused the recent expansion of the tropical Pacific OMZ. Considering future changes, however, these two influences may have very different trajectories: natural
climate variability could expand/contract the OMZ while the anthropogenic effect will depend on future economic development, air quality regulations and dust emissions\textsuperscript{27}. The interaction of these mechanisms and the effects of greenhouse forcing on the physical climate system\textsuperscript{28} will perturb the biogeochemistry and oxygenation state of the North Pacific Ocean with long term implications for subsurface [O\textsubscript{2}], nutrient cycling, and the marine ecosystem.


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Author contributions

TI and AN initiated the research. TI responsible for conducting ocean biogeochemistry simulations, analysis of the results and overall manuscript development. MSJ conducted atmospheric chemistry simulations. All authors contributed to the project planning, experimental design, the discussion of the results and their implications, as well as commenting on the manuscript.

Figure captions

Figure 1. Dissolved oxygen in the thermocline waters of the North Pacific

(A) Climatological distribution of [O₂] at the 435m depth based on the World Ocean Atlas 2009 in the units of μmol L⁻¹. (B) Oxygen change from 1970s to 1990s in the 20° longitude x 10° latitude x 100m depth bins based on Hydrobase329. The boxed regions indicate statistically significant O₂ change (90% confidence interval with two-tailed t-test with at least 20 profiles in each bin).

Figure 2. Pollution-induced deposition of soluble iron and fixed nitrogen based on GEOS-CHEM

(A) The increase in soluble iron deposition (molFe m⁻² s⁻¹) due to the atmospheric processing of aerosol dust with anthropogenic pollutants is plotted in the logarithmic scale. The plotted values are the difference between annual mean values of Year 2009 and the preindustrial condition. See supplementary material for the detailed model description. (B) The increase in fixed nitrogen deposition (molN m⁻² s⁻¹) due to anthropogenic pollutants.
Figure 3. Simulated changes in the oxygen and sinking organic flux from 1970s to 1990s

(A) Changes in [O₂] averaged over the depths of 260-710m in the units of μmol L⁻¹ based on our hindcast simulation. The difference was taken by subtracting the 1970-1979 averages from the 1990-1999 averages. (B) Changes in sinking organic carbon (Corg) flux evaluated at the 185m depth over the same time period. The data is plotted in the units of molC m⁻² yr⁻¹.

Figure 4. Breakdown of the simulated changes in the oxygen and sinking organic flux. The left column (A, C, E) is the oxygen changes and the right column (B, D, F) is the sinking organic flux, averaged at the same depth ranges in the same units. The top row (A, B) is the changes induced by the circulation variability, the middle row (C, D) is the changes induced by the pollution-enhanced sol-Fe deposition, and the bottom row (E, F) is the changes induced by the anthropogenic nitrogen deposition. Consistent color schemes are used.
Methods:

The aerosol soluble iron flux is calculated using the three-dimensional atmospheric chemical transport model GEOS-Chem (v8-01-01) coupled with a comprehensive dust-iron dissolution scheme. GEOS-Chem is driven by Goddard Earth Observing System (GEOS)-5 assimilated meteorology from the NASA Global Modeling Assimilation Office (GMAO) on a 2° × 2.5° (latitude – longitude) horizontal resolution and 47 vertical hybrid sigma-pressure levels. Soluble iron production during the atmospheric transport of mineral dust is calculated based on solid-, aqueous-, and gas-phase concentrations of relevant species along with the liquid-water content of the aerosol as a function of ambient relative humidity and temperature. The model explicitly considers solution nonidealities, proton- and organic (oxalate)-promoted iron dissolution processes, photochemical redox cycling between ferrous and ferric forms of iron, dissolution of different iron-containing minerals, and detailed mineralogy of wind-blown dust from the major desert regions. Present day soluble iron fluxes to the oceans are predicted in the model using current emission inventories for the year 2009, while pre-industrial fluxes are calculated by turning off all anthropogenic emission sources. Our calculation does not include combustion sources of soluble iron, so this is a lower bound of the impact of anthropogenic emissions on sol-Fe deposition. Even so, previous studies have shown that surface concentrations of mineral dust and soluble iron predicted by GEOS-Chem compare well with measurements over various oceanic regions and earlier modeling studies. The temporal evolution of the soluble iron inputs is calculated by interpolating between the present-day and pre-industrial conditions using the global coal production time series.
The ocean biogeochemistry model is based on the offline MITgcm using the data-constrained circulation fields previously used to study interannual variability of oxygen in the North Pacific\(^5\). In this study, the biogeochemistry model includes a representation of iron and macronutrient limitation as a Monod function of light, dissolved iron and macronutrient. The sources of iron include atmospheric deposition and diffusion from the sediments\(^6\) and its scavenging rates depend on the modeled particle concentration. Hydrothermal sources of iron are not included which is an important source for the deep waters\(^7\). We assume all soluble iron is released as dissolved inorganic iron (aggregate of ferric and ferrous) immediately upon deposition. Dissolved iron is subject to chelation with organic ligands\(^8\), and the free iron, unbound to ligands, is subject to the scavenging onto particles and is rapidly removed from the water column. The organic ligand concentration is set to a uniform constant at 1nM. The macronutrient increases with the deposition of fixed nitrogen. These aerosol fluxes as well as ocean circulation variability drive the evolution of the biological productivity and thermocline oxygen concentration. Since dissolved inorganic nitrogen (N) and dissolved inorganic phosphorus (P) are highly correlated in much of the oceans, N~16P, we represent N and P together as a single macronutrient pool, neglecting riverine input, nitrogen fixation, denitrification, and sedimentation. The net community production is parameterized as a product (not minimum) of Monod functions, and the simulated productivity is co-limited by macronutrient and iron in the tropical Pacific. The pollution-induced fixed nitrogen flux includes \(\text{NO}_3, \text{HNO}_3, \text{NO}_2, \) isoprene nitrates, \(\text{N}_2\text{O}_5,\) PANs, alkyl nitrates, \(\text{NH}_4,\) and \(\text{NH}_3\)\(^9\). Deposition of fixed nitrogen is applied as a source of this macronutrient in the surface ocean. Since we neglect these sources and sinks, the modeled macronutrient cycling is not closed and the macronutrient inventory slightly increases over time due to the anthropogenic input. The ocean productivity
may be biased in our calculation because, in a more realistic situation, increased atmospheric nitrogen input may shift the phytoplankton community structure towards non-nitrogen fixers due to the increased availability of fixed nitrogen, leading to a compensated change in the net community production. In contrast, increased sol-Fe deposition may increase the rate of nitrogen fixation\textsuperscript{10}. It is also possible that the denitrification may increase due to the expansion of tropical suboxic waters to balance the anthropogenic nitrogen input on a longer timescale.

The model source code as well as the output reported in this manuscript are archived at the corresponding authors’ institutional data server and is available upon request.

References for Methods section


a. Climatological oxygen at 435m depth [μmol L⁻¹] at 400m [μmol L⁻¹]

b. ΔO₂ (1990-1970) at 400m [μmol L⁻¹]
a. \( \Delta O_2 \) (1990s–1970s) [\( \mu \text{mol L}^{-1} \])

b. \( \Delta \) (sinking Corg flux), (1990s–1970s) [mol C m\(^{-2}\) yr\(^{-1}\)]
$\Delta O_2$ (1990s-1970s)

**Circulation effect**

- a.

**Fe effect**

- c.

**N effect**

- e.

$\Delta$ (Sinking Corg Flux)

- b.

- d.

- f.

$\Delta O_2$ (1990s–1970s) [μmol L$^{-1}$]

$\Delta$ Sinking Corg Flux (1990s–1970s) [mol C m$^{-2}$ yr$^{-1}$]