Anthropogenic processing of dust affects the oxygen content of the North Pacific Ocean

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Motivation: O$_2$ in the tropical Pacific is declining

- **Declining oxygen: ecosystem stress**
  - Coastal hypoxia
  - Expanding/Shoaling Oxygen Minimum Zone (OMZ)
    - Habitat compression / reorganization
  - Mass extinction events are associated with anoxia

- **Biogeochemical perturbation**
  - Redox chemistry of all major nutrients (N, P, Fe)
  - Denitrification, Fe reduction $\rightarrow$ nutrient budget
  - N$_2$O emissions go up *alot* $\rightarrow$ Greenhouse effect, stratospheric ozone
What controls subsurface $O_2$?

Subduction / Circulation

CFC-12 (Mecking et al., 2004)

Ocean productivity

SeaWiFS Chl-a

Physical $O_2$ supply (preformed $O_2$)

Productivity

$\rightarrow$ Respiration

$\rightarrow$ $O_2$ utilization
Current understanding: incomplete

- Warming: main suspect $\rightarrow$ Solubility decrease $\rightarrow$ $O_2$ decrease
- Weakening ocean vertical exchange
  $\rightarrow$ Weaker physical $O_2$ supply
  $\rightarrow$ Weaker nutrient upwelling $\rightarrow$ Weaker productivity

CMIP-5 multi-model ensemble (Cocco et al., 2013) support this

Ocean deoxygenation
EXCEPT FOR TROPICS

*Large model-model difference in tropics
“The tropical O$_2$ paradox”

Dissolved O$_2$ in the tropical thermocline has declined over the last several decades. However, warming simulations tend to show an opposite trend.

Possible (likely) reasons:

• Ocean mixing and eddies (Duteil and Oschlies, 2012; Gnanadesikan et al., 2007, 2012, 2013);

• Decadal variability (Deutsch et al., 2011; 2014)

• Missing critical biogeochemical processes?
  • Anthropogenic aerosol processing enhances nutrient input and eventually O$_2$ (Our hypothesis)
Mineral dust and Ocean Productivity

- Mineral dust is an important source of nutrients (Fe and P) to the (offshore) global ocean.
- It is the primary control of biological productivity for areas which are limited by iron.
- Dust interaction with pollution can affect the soluble (bioavailable) fraction of Fe, P in dust (and reactive N).

![Diagram showing the distribution of Fe or P in dust, with labels for Total Fe or P and Soluble (bioavailable) Fe or P.](image)
Dust Fe solubility: pH-dependent

**pH range for sufficient iron dissolution** (found in pollution, Weber et al., 2016)

- $\log K_1 = 1.88$ (Baes and Mesmer, 1976; $l=0$
- $\log K_1 = 0.09$ (Lindsay, 1979; $l=0$
- $\log K_1 = 1.69$ (Tardy and Nahon, 1985; $l=0$
- $\log K_1 = 1.69, l=0.26$ mole/kg

Iron dissolution rate in dust:

<table>
<thead>
<tr>
<th>pH</th>
<th>$\log(Fe(\text{mol/kg}))$</th>
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<td>14.0</td>
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Seawater pH

Meskhidze et al., 2003
How does pollution increase the fraction of soluble Fe,P in dust?

Cloud processing

- Atmosphereric emission
  - Dust → SO₂, HNO₃
  - Dust → Organic acids

Cloud water
- pH ~ 6
- More production of strong organic acids, sulfate, nitrate

Clear-sky processing

- Cycling
  - Dust
- Aerosol water
- pH ~ 0-2

Region of Fe,P dissolution
Dust is emitted close to “pollution”: opportunity for interaction

Dryland Systems
- Hyper-arid
- Arid
- Semi-arid
- Dry subhumid

Source: Millennium Ecosystem Assessment

Drylands are home to 34.7% of the global population in 2000.
Predicting aerosol pH and liquid water

What we need to know:

• Total concentration of aerosol “precursors” (like \( \text{NH}_3 \), \( \text{HNO}_3 \), \( \text{HCl} \), \( \text{H}_2\text{SO}_4 \), \( \text{Na} \), organic precursors) – or a subset of them
• Ambient conditions (e.g., relative humidity, temperature)

Compute the:

• number of phases that develop in the aerosol
• the chemical composition of the aerosol and gas phases.

At thermodynamic equilibrium.

We always need to know it when modelling the aerosol evolution (it provides the “driving force” for mass transfer).
Aerosol components needing consideration

Some inorganic components:
- Ammonium sulfate & bisulfate
- Sulfuric acid
- Seasalt (NaCl)
- Crustal material (CaCO$_3$, Mg & K salts)
- Nitrate salts (NH$_4$NO$_3$, NaNO$_3$)
- Chloride salts (KCl, NH$_4$Cl)
**Solid phase:** NaHSO$_4$, NH$_4$HSO$_4$, Na$_2$SO$_4$, NaCl, (NH$_4$)$_2$SO$_4$, (NH$_4$)$_3$H(SO$_4$)$_2$, NH$_4$NO$_3$, NH$_4$Cl, NaNO$_3$, K$_2$SO$_4$, KHSO$_4$, KNO$_3$, KCl, CaSO$_4$, Ca(NO$_3$)$_2$, CaCl$_2$, MgSO$_4$, MgCl$_2$, Mg(NO$_3$)$_2$

Species in **bold** were introduced in ISORROPIA II (Fountoukis and Nenes, 2007)

**Liquid phase:** Na$^+$, NH$_4^+$, H$^+$, OH$^-$, HSO$_4^-$, SO$_4^{2-}$, NO$_3^-$, Cl$^-$, H$_2$O, HNO$_3$(aq), HCl(aq), NH$_3$(aq), Ca$^{2+}$, K$^+$, Mg$^{2+}$

**Gas phase:** HNO$_3$, HCl, NH$_3$, H$_2$O

http://nenes.eas.gatech.edu/ISORROPIA
Comprehensive atmospheric dust transport and processing model (GEOS-Chem/DFeS)

- 3-D Global Chemistry Transport Model
- Full chemistry configuration
- GEOS-5 meteorology
  - Goddard Earth Observing System (GEOS) of the NASA Global Modeling Assimilation Office
- Detailed emission inventories
  - Fossil fuel, biomass burning, biofuel burning, biogenic and anthropogenic aerosol emissions
- State-of-the-art transport (TPCORE) and photolysis (FAST–J) routines
- $2^\circ \times 2.5^\circ$, 47 vertical grids

Mineral Dust and Sol-nutrient Treatment
- DEAD emission scheme
  - GOCART source function
- **Soluble iron (Sol-Fe) dissolution**
  - prognostic acid-based dust-Fe dissolution scheme (Meskhidze et al., 2003; Johnson et al., 2010)
  - Fe(II)/Fe(III) redox cycling
  - Organic (oxalate) promoted Fe dissolution
  - Photochemistry
  - Different Fe containing minerals
- **Soluble phosphorus (Sol-P) dissolution**
  - acid based (Nenes et al., 2011)
- **Seven major individual dust sources**
  - North Africa, South Africa, North America, Asia, Australia, the Middle East, and South America

Johnson & Meskhidze, GMD (2013)
Also Myriokefalitakis et al., Biog. (2015)
Apply GEOS-Chem/DFeS to compute Fe flux to the surface ocean

- Focus on the impact of pollution on soluble Fe flux
  - Preindustrial simulation (no pollutants)
  - Contemporary simulations (2009 equivalent emissions)

(Anthro) – (Natural) shows x3 increase in soluble Fe flux of North Pacific
Ocean response to changing Fe flux

• Offline ocean biogeochemistry model (MITgcm - ECCO)
  – Global 1°x1° with 23 z levels + seaice model assimilated with a suite of satellite and in-situ observation (Wunsch and Heimbach, 2007)

• 2 types of biogeochemistry models
  – Simple biogeochemistry: nutrient only (P, Fe, Parekh et al., 2005)
  – Ecosystem: functional group model (Dutkiewicz et al., 2005)
    • Both models are driven by the variable Fe solubility
Biological carbon export stimulated by anthropogenic dust processing

- Pre-industrial spin up (~ 500 years)
- Use climatological circulation in all runs (no ocean circ. variability)
- Control vs anthropogenic run: linearly transition from pre-industrial to contemporary condition over 100 years.

**Long-term response of $C_{\text{org}}$ export**

- Subtropical carbon export weakens in the subtropics → N, P limitation
- Tropical carbon export strengthens in the HNLC regions → Fe limitation
Multi-decadal oxygen response consistent with obs

a. Observation

b. Model

Table: Delta O2 (1990-1970) at 400m [uM]

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Table: Delta O2 (modern) - (pre-ind) : mmol/m3

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C. Time rate of O2 change: mmol/m3/yr

D. Fractional change in hypoxic volume: %

- BGC
- ECO
How does the modified Fe flux affect O$_2$?
How does the modified Fe flux affect $O_2$?
How does the modified Fe flux affect $O_2$?
How does the modified Fe flux affect $O_2$?
How does the modified Fe flux affect O₂?
How does the modified Fe flux affect $O_2$?

One mechanism can explain the pattern in observed $O_2$.!
The tropical $O_2$ paradox still remains

- The cause of recent expansion of tropical Pacific OMZ is still under debate
  - Decadal climate variability: negative phase of the PDO index since 1990s
    - This trend will eventually flip and then OMZ will shrink back?!
  - Air pollution: a trend that is “on top” of natural variability
    - Deposition of polluted dust may continue to decline in observed $O_2$
    - Future trajectory depends on emission regulations

- More questions
  - When will we observe global warming effects?
  - What about P deposition?
  - Implications for geoengineering and carbon management
  - Can this explain massive extinction events during intense volcanic activity periods of the past?
THANK YOU!