Thermodynamic constraints imposed by ocean acidification on respiration by marine animals.

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Ocean acidification from the invasion of fossil fuel CO₂ at the sea surface and from climate induced reduced ventilation (increased respiratory CO₂) at depth poses a challenge to marine life. The most obvious effect is from the reduction in dissolved carbonate ion affecting carbonate shell formation, and coral reef impacts are widely predicted. But higher oceanic CO₂ levels can also impose a stress on general metabolic capacity of all higher animals, yet we have no formal numerical means of expressing the combined impacts of elevated CO₂ and lower O₂ levels. We suggest that the simplest form of the energy balance of the basic respiration equation:

$$\Delta G = \Delta G^\circ - RT \ln \left\{ \frac{[\text{CO}_2]}{[\text{Corg}] \cdot [\text{O}_2]} \right\}$$

provides a useful tool for quantifying this stress. From this we define a simple respiration index:

$$RI = \log_{10} \left( \frac{p_{O_2}}{p_{CO_2}} \right)$$

in which the pO₂:pCO₂ ratio defines the ability to gain energy from the respiration process from a constant food source.

The greater part of the world’s ocean waters are sufficiently well oxygenated that the anticipated higher CO₂ levels will not cause significant stress. But in already oxygen deficient regions this term becomes significant. We show that sub-oxic and anoxic conditions will not only expand laterally, but vertically as well. These expanding sub-oxic zones will present an ever increasing challenge to the diurnal vertical migration of all organisms from zooplankton to fish. And where these areas intersect the coast and the continental shelf, the so called "dead zones" inhospitable to aerobic life will greatly expand.
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Ocean acidification –
Global warming’s sour sibling

- Ocean fossil fuel CO$_2$ burden is now greater than 530 billion tons.
- Invasion rate ~1 million tons/hour
- Surface ocean pH lower by 0.1 pH today
- Under IPCC “Business as Usual” lower by ~0.4 pH by 2100 (Caldeira & Wickett, 2003).
- Loss of 55% carbonate ion in surface waters, affecting calcifying organisms and coral reefs
- Calcification problem is not the only issue...

Sources and consequences of ocean acidification

- At least 3 sources of OA:
  - Fossil fuel CO$_2$ invasion.
  - Acidic emissions from ships and power plants (commonly known as acid rain).
  - Reduced ventilation / decreased O$_2$ levels.
- Consequences:
  - Declining [CO$_3$$^-$] / calcification rates.
  - Inhibition of respiration rates in mid-water organisms.
  - An ocean that is more transparent to sound.
- Theoretical and experimental challenges:
  - Can we correctly simulate an ocean with higher CO$_2$, lower O$_2$ and global/ocean warming?

Impact of reduced ventilation

The pH changes from adding fossil fuel CO$_2$ and from increased respiration, are closely similar after the full Redfield equation is used. The effects are larger in the Pacific mid-waters due to the lower buffer capacity of these waters.

Oceanic O$_2$ levels have been on the decline for some time...

- Trends to anoxia first detected in the Baltic early in the 20th century – and the deep basins are permanently anoxic.
- Seasonally anoxic waters appeared on the continental shelf off the coast of New Jersey beginning in the 1980s.
- Large-scale seasonal anoxia now occurs in the shallow Gulf of Mexico.
- Seasonally anoxic waters appeared off Oregon in 2005.
- Trends to anoxia are readily detectable in the deep water in the Sea of Japan.
- The tropical oceans low O$_2$/high CO$_2$ zones are increasing in size, and O$_2$ levels are declining.

The global pH trend is a combination of the downward penetration of the fossil fuel signal, and the emergence of the respiration CO$_2$/pH signal at depth resulting from reduced ventilation. These two effects are rapidly merging in a “perfect storm”:

Total CO$_2$ change over 15 years in the Pacific

CO$_2$ change due to ventilation and respiration processes

CO$_2$ change due to anthropogenic CO$_2$

Sabine et al. (pers. comm.)

Impact of reduced ventilation

- Fossil Fuel impact
- Organic Matter oxidation

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A simple physiological view of pH and the impact of enhanced levels of CO₂

From Portner (2008).

Can we translate the problem into a "global change" number?

- External ocean geochemical signals are the driver for models and we measure and predict these fields.
- Animals have differing tolerances for low O₂/high CO₂ environments, but some common principles are at work — we need to identify these.
- The use of pH alone as a model variable is incomplete since the traditional relationship between O₂-CO₂-pH in the ocean that is defined by the Redfield ratio is now breaking down due to the fossil fuel CO₂ invasion.
- We are groping for a multi-D map of fitness as marine animals experience a changing T-O₂-CO₂ world.

CO₂, O₂ & T are thermodynamically linked:

The most basic respiration equation is:

\[ \text{C}_{\text{org}} + \text{O}_2 \rightarrow \text{CO}_2 \]

- For which one can write the Gibbs Free Energy equation:
  \[ \Delta G^\circ = -RT \ln \left( \frac{f_{\text{CO}_2}}{f_{\text{O}_2}} \right) \]
- Marine organisms use a variety of organic matter types, but the term \( \ln \left( \frac{f_{\text{CO}_2}}{f_{\text{O}_2}} \right) \) is constant throughout and is T dependent.
- So, by rearranging terms, etc:
  \[ \text{Respiration Index} = \text{Log}_{10} \left( \frac{\text{pO}_2}{\text{pCO}_2} \right) \]
- This term is linear in energy gained from respiration, and changing pCO₂ or pO₂ will change the energy available.

Deep-water amplification of pCO₂ signal

Example: a deep water station off Central America with v-low pO₂ & high pCO₂

Increase pCO₂ 280 μatm at surface yields +1300 μatm at 600m at equilibrium.

Increase pCO₂ 560 μatm at surface yields +2600 μatm at 600m at equilibrium.
Daily Vertical Migration = largest animal migration on Earth
Daytime deep to escape predation, but in low pH water

Some important caveats:
- The examples presented here minimized the impacts since we have examined only the direct CO₂ effects for simplicity:
  - We have used constant temperature, and we expect significant warming (this will raise the pCO₂ further).
  - We have used simple addition of CO₂ levels, not a GCM.
  - We have used constant O₂ levels, and O₂ levels are decreasing world-wide thus putting further stress on the ecosystem.
  - The effects are large enough with just the pH and pCO₂ changes in the mid-water and deep water that large changes in the marine ecosystems seems possible from CO₂ alone.
- We lack some basic experimental and conceptual tools for examining this, but they are rapidly being developed.

Summary and Conclusions:
- Geologically extraordinary oceanic CO₂ levels are very likely to occur, and the effects are generally negative for marine life.
- Effects on calcifying systems such as coral reefs and calcareous plankton can be estimated – but we have no such general principle for estimating effects on other marine animals.
- It is possible to construct a function combining CO₂ and O₂ levels that can represent aerobic functioning: the respiration index (RI).
- Future high CO₂ levels may be tolerable for many animals in well oxygenated water but there will be reduced energy and lower thermal tolerance for marine ecosystems world-wide.
- We may expect large expansions of the “sub-oxic zones” in the Pacific and Indian Oceans, and in other regions (especially highly productive coastal areas) from changing CO₂ alone.
- When combined with the impact that reduced ventilation has on O₂ concentrations the effects are greatly magnified.

Some overall comments:
- These are crude, short term, experiments providing only visual information.
- The dissolved O₂ levels encountered were about 10 µmoles/kg, and thus high pCO₂ levels had to be created to force a 3:1 ratio. We will not see ocean pCO₂ levels this high under any foreseeable scenario.
- BUT a change of only 5 µmoles/kg in deep-sea O₂ here halves the pCO₂ required to achieve this ratio, and that is very possible.
- Experiments to test the impacts of other pO₂:pCO₂ ratios will have to be much more sophisticated and engage physiologists and microbiologists.