Gas solubility and exchange: How and why gases move in and out of the ocean

S. Bushinsky, 2010

Why are gases useful?

- Tracers for physical processes:
 - mixing, deep water formation, air-sea exchange, circulation
- Biological processes: biological production, respiration, oxygen deficient zones
- Atmospheric chemistry/global climate change
- Tracers of large-scale ocean changes

What controls gas concentrations?

- Air-sea gas exchange + solubility
- Production and removal within the ocean
- Mixing in the ocean



Atmosheric Fraction

Composition of the atmosphere

Table 1.5.The major gases of the atmosphere excluding water vapor,
which has a concentration of a few percent at saturation in the
atmosphere

Seawater equilibrium concentrations were calculated from the Henry's Law coefficients at 20 °C and S = 35.

Gas	Atmospheric mole fraction (atm)	Seawater equilibrium concentration (µmol kg ⁻¹)
N_2 O_2 Ar CO_2 Ne He Kr Xe	7.808×10^{-1} 2.095×10^{-1} 9.34×10^{-3} 3.65×10^{-4} 18.2×10^{-6} 5.24×10^{-6} 1.14×10^{-6} 0.87×10^{-7}	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

Mole fraction is the amount (atm or moles) of a gas relative to atmosphere as a whole

Emerson and Hedges, 2007



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Seawater Concentration

N2

Dalton's law of partial pressures

- Partial pressure (p_i) is the pressure of an individual gas:
 - So if oxygen is ~20% of atmospheric pressure, and atmospheric pressure is latm, the partial pressure of oxygen is 0.2 atm
- Total pressure in a fixed volume is equal to the sum of the partial pressures of the components of the mixture

$$P_T = \sum p_G = p_{N_2} + pO_2 + pAr + pH_2O + \cdots$$

• Dalton's Law implies ideal behavior, i.e. all gases behave independently of one another.

Gas solubility

- The solubility of a gas determines its partitioning between the atmosphere and water
 - The amount of a gas that will be present in water at a given T and $P_{\rm T}$ (total atmospheric/headspace pressure)
- Solubility coefficients are a type of chemical equilibrium constant that defines the solubility of a gas in water

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Solubility vs. partial pressure: O_2 and N_2

- Oxygen: ~20 % of the atmosphere Partial pressure = 0.209
- Nitrogen: ~78 % of the atmosphere Partial pressure = 0.781

Solubility vs. Temperature



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 N_2 is 4x more plentiful in the atmosphere, but only half as soluble as oxygen, so saturation concentration is ~2x oxygen





What affects gas exchange in the ocean?



Mechanisms?

- Cooling/heating
- Mixing with deeper waters
- Breaking waves
- Winds
- wind speed
- wave height
- wave shape
- breaking vs. non-breaking (bubbles)
- spray
- relative direction of wind and waves



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Gas solubility and exchange: Key points

- Gases move toward equilibrium between the atmosphere and ocean
- The partial pressure of a gas in the atmosphere and the solubility of the ocean water determine how much gas the ocean can hold
- Once there is a difference between the actual concentration in the water and how much gas the water can hold, gas exchange occurs
 Faster with high winds, breaking waves