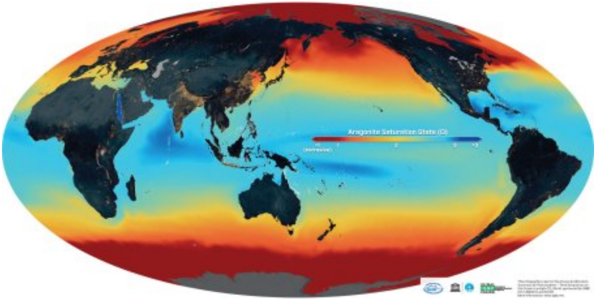
Acid Pollution of Natural Waters



Outline of Topics

Lecture Question: Acids and Bases

What is an acid? What is a base?

Consider a reaction

$$HA + B \longrightarrow A^- + HB^+$$

- An acid is a proton donor; in the above reaction this is HA
- A base is a proton acceptor, B in the above reaction
- When an acid donates a proton, it loses an H atom and its charge decreases by one. In the above equation, $HA \rightarrow A^-$
- When a base accepts a a proton, it gains an H atom and its charge increases by one: $B \rightarrow HB^+$
- Reaction between acid and base is also called a *neutralization reaction*

Strong and Weak Acids and Bases

What is the difference between a strong and weak acid or base?

- Quick answer: they have a bigger impact on pH, other things being equal
- Acids react with water to form hydronium ion: $HA + H_2O \longrightarrow A^- + H_3O^+$
- Bases react to form hydroxide ion: $B + H_2O \longrightarrow HB^+ + OH^-$
- Weak acids/bases do not react completely with water but are involved in a **chemical equilibrium**.

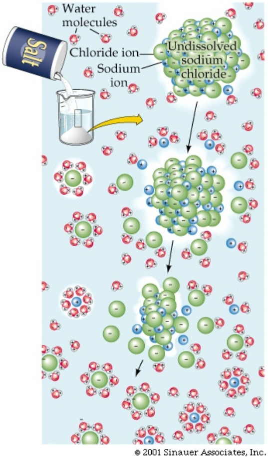
$$HA + H_2O \rightleftharpoons A^- + H_3O^+ \qquad \text{(acid dissociation)}$$

$$B + H_2O \rightleftharpoons HB^+ + OH^- \qquad \text{(base dissociation)}$$

- Three common strong acids: HCl, H_2SO_4, HNO_3. An important weak acid: H_2CO_3
- Four common strong bases: NaOH, KOH, $Ca(OH)_2$, $Mg(OH)_2$. An important weak base: NH_3

Chemical Equilibrium

Explain chemical equilibrium using dissolution of calcium carbonate, $CaCO_3$, as an example.



- Left figure is dissolution

  $$CaCO_3(s) \longrightarrow Ca^{2+} + {CO_3}^{2-}$$

- Right figure is precipitation

  $$Ca^{2+} + {CO_3}^{2-} \longrightarrow CaCO_3(s)$$

- Together:
  $Ca^{2+} + {CO_3}^{2-} \rightleftharpoons CaCO_3$

Chemical Equilibrium

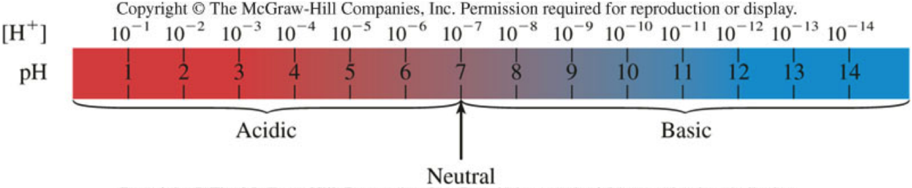
A chemical equilibrium is a *dynamic* equilibrium. What does that mean?

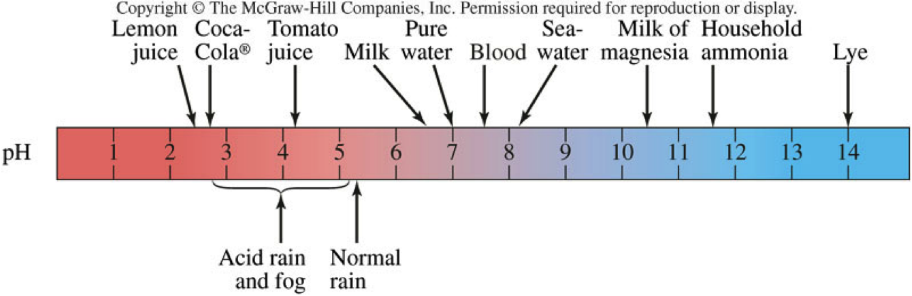
How does the equilibrium respond to a change in concentration?

- Illustrate with $CaCO_3(s) \rightleftharpoons Ca^{2+} + {CO_3}^{2-}$.
- Double arrows signify that two chemical reactions are occurring: forward (dissolution) and reverse (precipitation)
- Dynamic equilibrium means both are occuring at the same rate, resulting in steady state concentrations. Doesn't mean nothing is happening.
- A change will change one or both rates, and the reaction will shift in response. Examples:
  - adding ${CO_3}^{2-}$ will increase rate of precipitation and shift rxn to the *left* (more will precipitate)
  - adding acid will react with ${CO_3}^{2-}$ (a base), decreasing rate of precipitation and shift rxn to the *right* (more will dissolve)
- Le Chatelier's principle can help with predictions.

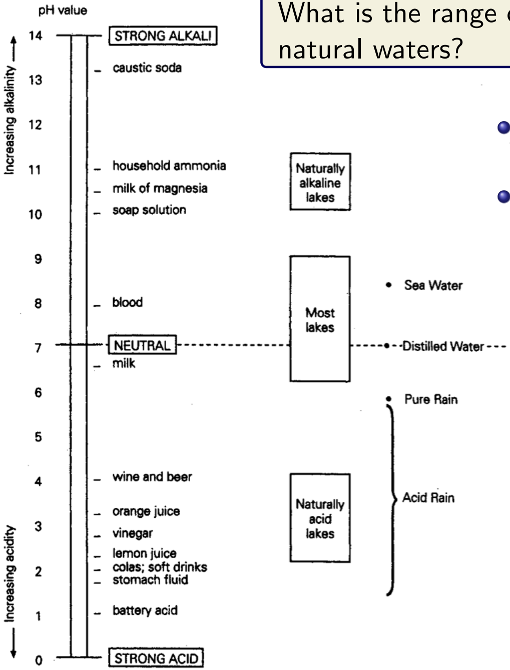
Lecture Question: The pH Scale

Explain the pH scale of acidity.





What is the range of 'normal' pH values for natural waters?



- Most lakes alkaline, pH 6.5–8.5, due to mineral bases like $CaCO_3$
- Pure rain in naturally acidic due to atmospheric CO_2, which dissolves to form carbonic acid

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

'Acid rain' means more acidic than this, pH < 5.6

Acid Deposition (Review)

Remind me: how do human activities case acid deposition?

- Photochemical oxidation of SO_2 and NOx emissions
  - $SO_2(g) \xrightarrow{OH, O_3} H_2SO_4 \xrightarrow{NH_3} (NH_4)_2SO_4(s)$
  - $NO(g) \xrightarrow{OH} HNO_3 \xrightarrow{NH_3} NH_4NO_3(s)$
  - Note that initial produce is a strong acid, which forms PM through an acid-base neutralization rxn. However, PM is still acidic.
  - wet and dry deposition

Acid Mine Drainage

How does mining lead to acid pollution?

- Hard rock mining operations can expose minerals and mine waste to air and water
- Acid mine drainage mostly due to the *biologically-mediated oxidation of pyrite*, FeS_2

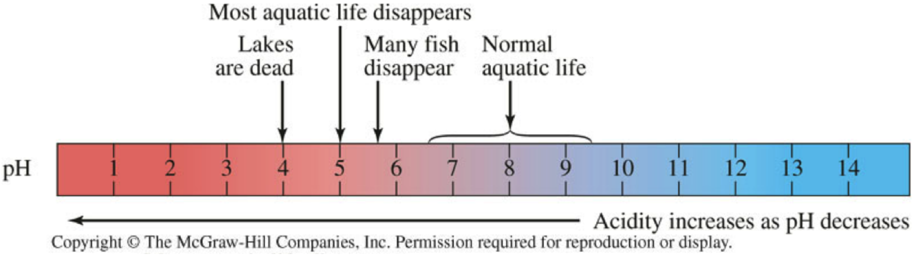
$$FeS_2 + O_2 + H_2O \longrightarrow Fe(OH)_3 + H_2SO_4$$

(Note: chemical equation is unbalanced.)

- Color is due to precipitation of oxidized iron (eg as $Fe(OH)_3$)

Effects on Aquatic Ecosystems

What are the possible effects of acid pollution on aquatic ecosystems?



- *Acute effects*: osmoregulation, toxic metal mobilization (Al, Mg, Zn)
- *Chronic effects*: reproduction problems
  - lowers calcium levels in female fish, hinders ability to produce eggs
  - fertilized fish eggs may develop abnormally
  - frog and salamander eggs can be greatly affected by spring snowmelt
- *Ecosystem effects*:
  - can result in decline and algal species diversity and biomass
  - may effect ecosystem productivity
  - may decrease decomposer populations, affecting nutrient cycling and increasing DOM/POM levels

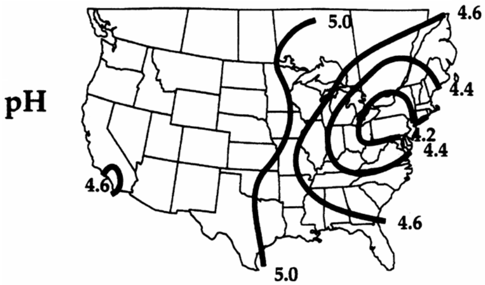
Effects on Terrestrial Ecosystems

What are the possible effects of acid pollution on terrestrial ecosystems?

- Direct Effects: damage to foliage
- Effects on Soil
  - The nature of soil
  - Soil pH
  - Loss of nutrients and other metals
  - Loss of ability to retain nutrients

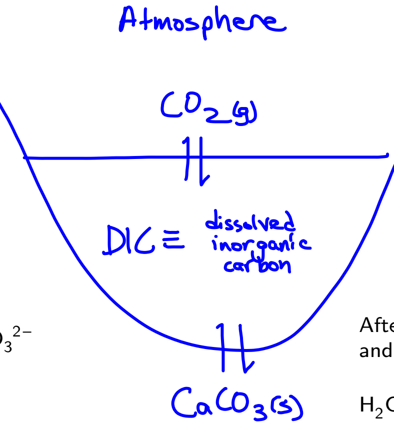
Buffering of Acid Pollution

Are some areas more sensitive than others to acid pollution?



- Overlay acidity of precipitation with shaded areas that are not well buffered to acid pollution. Pollution from power plants in midwestern states acidifies lakes/rivers/soils in northeastern states.
- Similarly, emissions from Great Britain cause acid pollution in Scandinavian countries.

Explain the carbonate chemistry of natural waters.



Dissolution of CO_2

$CO_2 + H_2O \rightleftharpoons H_2CO_3$

DIC is H_2CO_3, HCO_3^-, CO_3^{2-}

Dissolution of $CaCO_3$

$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$

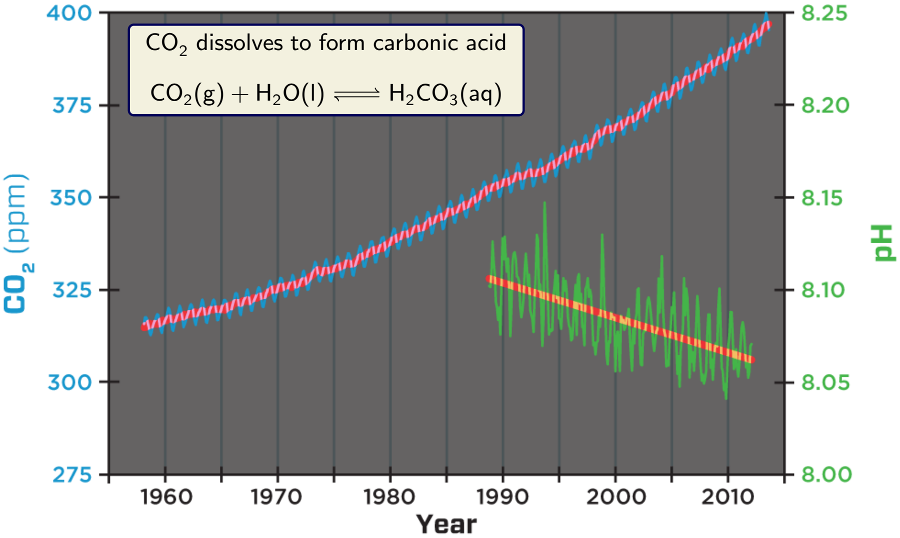
After dissolution, carbonic acid and carbonate react:

$H_2CO_3 + CO_3^{2-} \rightleftharpoons 2\,HCO_3^-$

The result of the above is the following net rxn, which can be viewed as an acid-base rxn between CO_2 in air and $CaCO_3$ mineral:

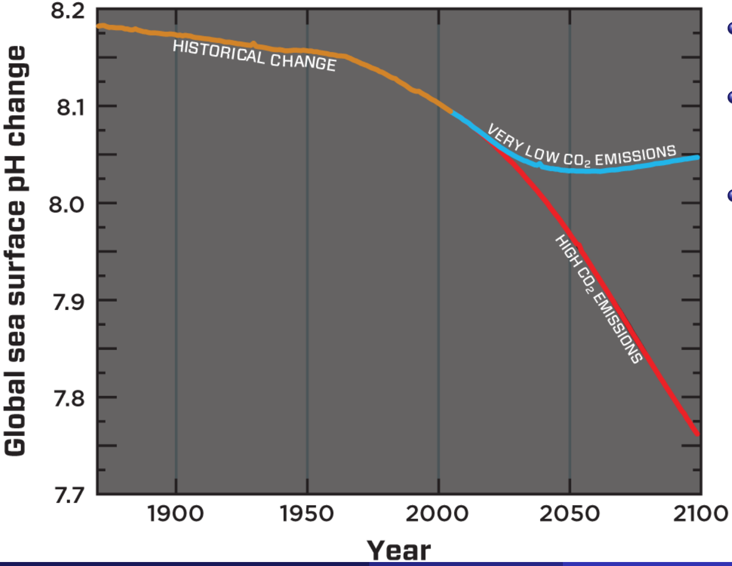
$$CO_2(g) + CaCO_3(s) + H_2O(l) \rightleftharpoons Ca^{2+}(aq) + 2\,HCO_3^-(aq)$$

What causes ocean acidification, and how much has the ocean acidified?



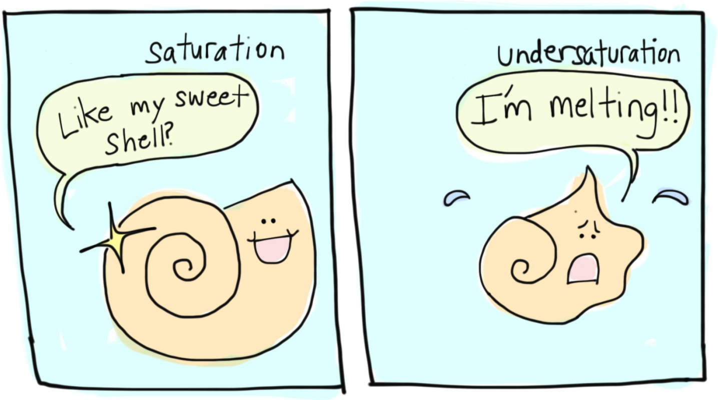
Projected Acidification

How much more is the ocean expected to be acidified?



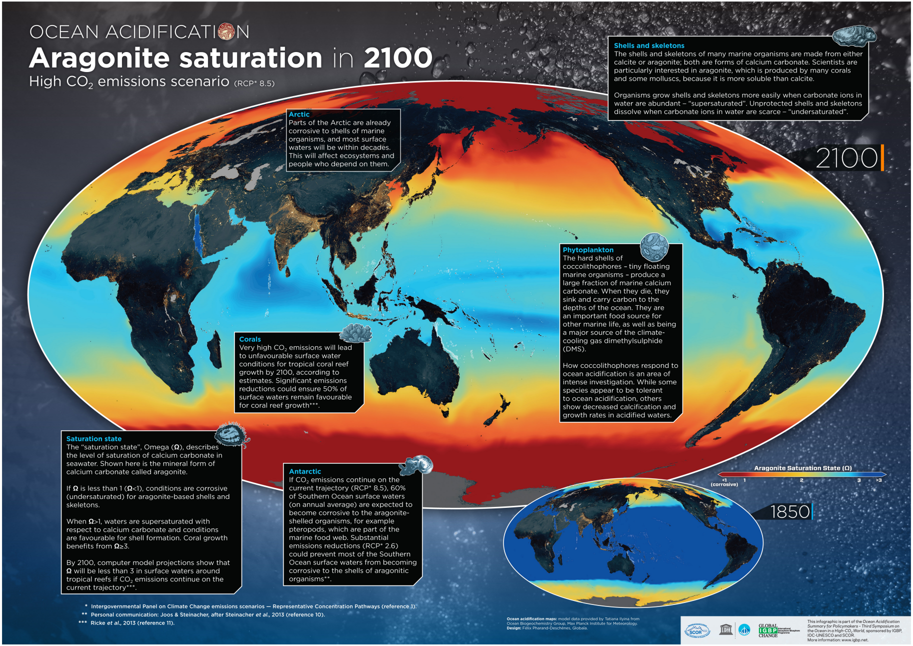
- Depends on future emissions
- Optimistic pH in 2100: 8.05 (41% increase in H^+)
- Pessimistic pH: 7.75 (180% increase)

Why should we care about ocean acidification?

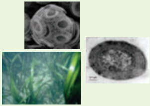
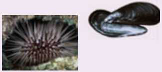


Effect of pH on $CaCO_3$ equilibrium:

$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3{}^{2-}(aq)$



OCEAN ACIDIFICATION
Aragonite saturation in 2100
High CO_2 emissions scenario (RCP* 8.5)
Shells and skeletons
The shells and skeletons of many marine organisms are made from either calcite or aragonite; both are forms of calcium carbonate. Scientists are particularly interested in aragonite, which is produced by many corals and some molluscs, because it is more soluble than calcite.
Organisms grow shells and skeletons more easily when carbonate ions in water are abundant – "supersaturated". Unprotected shells and skeletons dissolve when carbonate ions in water are scarce – "undersaturated".
Arctic
Parts of the Arctic are already corrosive to shells of marine organisms, and most surface waters will be within decades. This will affect ecosystems and people who depend on them.
2100
Phytoplankton
The hard shells of coccolithophores – tiny floating marine organisms – produce a large fraction of marine calcium carbonate. When they die, they sink and carry carbon to the depths of the ocean. They are an important food source for other marine life, as well as being a major source of the climate-cooling gas dimethylsulphide (DMS).
How coccolithophores respond to ocean acidification is an area of intense investigation. While some species appear to be tolerant to ocean acidification, others show decreased calcification and growth rates in acidified waters.
Corals
Very high CO_2 emissions will lead to unfavourable surface water conditions for tropical coral reef growth by 2100, according to estimates. Significant emissions reductions could ensure 50% of surface waters remain favourable for coral reef growth***.
Saturation state
The "saturation state", Omega (Ω), describes the level of saturation of calcium carbonate in seawater. Shown here is the mineral form of calcium carbonate called aragonite.
If Ω is less than 1 (Ω<1), conditions are corrosive (undersaturated) for aragonite-based shells and skeletons.
When Ω>1, waters are supersaturated with respect to calcium carbonate and conditions are favourable for shell formation. Coral growth benefits from $\Omega \geq 3$.
By 2100, computer model projections show that Ω will be less than 3 in surface waters around tropical reefs if CO_2 emissions continue on the current trajectory***.
Antarctic
If CO_2 emissions continue on the current trajectory (RCP* 8.5), 60% of Southern Ocean surface waters (on annual average) are expected to become corrosive to the aragonite-shelled organisms, for example pteropods, which are part of the marine food web. Substantial emissions reductions (RCP* 2.6) could prevent most of the Southern Ocean surface waters from becoming corrosive to the shells of aragonitic organisms**.
Aragonite Saturation State (Ω)
<1 (corrosive)
1
2
3
>3
1850
* Intergovernmental Panel on Climate Change emissions scenarios — Representative Concentration Pathways (reference 1).
** Personal communication: Joos & Steinacher, after Steinacher et al., 2013 (reference 10).
*** Ricke et al., 2013 (reference 11).
Ocean acidification maps: model data provided by Tatiana Ilyina from Ocean Biogeochemistry Group, Max Planck Institute for Meteorology.
Design: Félix Pharand-Deschênes, Globaïa.
This infographic is part of the Ocean Acidification Summary for Policymakers – Third Symposium on the Ocean in a High-CO_2 World, sponsored by IGBP, IOC-UNESCO and SCOR.
More information: www.igbp.net.

Physiological response	Major group	Species studied	Response to increasing CO_2: a	b	c	d
Calcification 						
	Coccolithophores[1]	4	2	1	1	1
	Planktonic Foraminifera	2	2	–	–	–
	Molluscs	4	4	–	–	–
	Echinoderms[1]	3	2	1	–	–
	Tropical corals	11	11	–	–	–
	Coralline red algae	1	1	–	–	–
Photosynthesis[2] 						
	Coccolithophores[3]	2	–	2	2	–
	Prokaryotes	2	–	–	1	–
	Seagrasses	5	–	–	–	–
Nitrogen Fixation 						
	Cyanobacteria	1	–	1	–	–
Reproduction 						
	Molluscs	4	4	–	–	–
	Echinoderms	1	1	–	–	–

1) Increased calcification had substantial physiological cost; 2) Strong interactive effects with nutrient and trace metal availability, light, and temperature; 3) Under nutrient replete conditions.