Surface Waters and Acidification
Water Pollution II

- Surface Water Eutrophication
- Acidification of Lakes
  - Chemistry
  - Observations of Ion Concentrations
  - Mobilization of Metals
Surface Water Quality

- In 1972, when the Clean Water Act was enacted, ~90% of surface water in the US wasn’t fishable or swimmable (one or the other or both)!

- As of 1992, 38% of rivers and 44% of surface water in the US was not fishable or swimmable, due to nutrients, pesticides, oxygen demanding wastes, metals, etc.

- 2001: 35% of rivers and 45% of lakes
Lakes and Reservoirs

- Eutrophication: A natural lake aging process that can take 1000’s of years.
  - Accumulation of silt and organic matter eventually fills in lakes
  - Process can be accelerated by human activities and is currently affecting about half of US lakes.

- Oligotrophic Lake: Young lake with few nutrients and low plant productivity.
• Euphotic zone: The upper layer of a lake where plants produce more oxygen than they consume by respiration.

• Profundal zone: The layer below the euphotic zone.

→ At the euphotic/profundal boundary, the light is ~1% of the sunlight hitting the lake surface.
Most effective way to control eutrophication: *Remove the limiting nutrient*

In fresh water, nitrogen (as nitrate) is usually not limiting, since

a) it is deposited from the polluted atmosphere and

b) blue-green algae, which (together with rhizobial bacteria) can fix \( \text{N}_2 \) from the atmosphere, are common in eutrophying lakes.
Nitrate: $N_2$ bond is too strong for most organisms to use.

A chemical representation of algal photosynthesis:

$$106\text{CO}_2 + 16\text{NO}_3^- + \text{H}_3\text{PO}_4^{2-} + 122\text{H}_2\text{O} + 18\text{H}^+ \rightarrow$$

$$\text{C}_{106}\text{H}_{263}\text{O}_{110}\text{N}_{16}\text{P} + 138\text{O}_2$$

$$\frac{\text{mass N}}{\text{mass P}} = \frac{16 \times 14}{31} = 7.22$$
N/P > 10, water is phosphorous limited.
N/P < 5, water is nitrogen limited.

FIGURE 5.19  Well-mixed lake phosphorus mass balance.
Phosphorus of less than 0.01 mg/L generally does not promote excessive algal growth.

Writing the mass balance:

\[ \text{addition of } P = \text{removal of } P \]

\[ QC_{in} + S = QC + v_s AC \]

- \( S \) = rate of addition of \( P \) from a point source
- \( C \) = Concentration of \( P \) in the lake
- \( C_{in} \) = " incoming stream flow
- \( v_s \) = the settling rate of \( P \) (m/s)
- \( A \) = surface area of the lake

Rearranging we have:

\[ C = \frac{QC_{in} + S}{Q + v_s A} \]
Example 1

A phosphorus-limited lake with a surface area of $80 \times 10^6 \text{ m}^2$ is fed by a $15 \text{ m}^3/\text{s}$ stream that has a phosphorus concentration of $0.01 \text{ mg/L}$. In addition, effluent from a point source adds $1 \text{ g/s}$ of phosphorus. The phosphorus settling rate is $10 \text{ m/yr}$. What is the phosphorus concentration, and will it be contributing to eutrophication?

\[
C = \frac{QC_{in} + S}{Q + v_s A}
\]

\[
QC_{in} = \left(15 \frac{\text{m}^3}{\text{s}}\right)\left(0.01 \frac{\text{mg}}{\ell}\right)\left(10^{-3} \frac{\text{g}}{\text{mg}}\right) = 0.15 \frac{\text{g}}{\text{s}}
\]

\[
S = 1 \frac{\text{g}}{\text{s}}
\]
\[ V_s = \frac{10 \text{ m/yr}}{(365 \text{ day/yr})(24 \text{ hr/day})(3600 \text{ s/hr})} = 3.17 \times 10^{-7} \text{ m/s} \]

\[ C = \frac{Q C_{in} + S}{Q + v_s A} = \frac{0.15 \text{ g/s} + 1 \text{ g/s}}{15 \text{ m}^3/\text{s} + (3.17 \times 10^{-7} \text{ m/s})(80 \times 10^6 \text{ m}^2)} \]

\[ = 0.028 \ \frac{g}{\text{m}^3} = 0.028 \ \frac{\text{mg}}{\ell} \]
Acidification of Lakes

- Acid rain → acidification of lakes

- Acid deposition results from emissions of sulfur and nitrogen oxides (SO$_x$, NO$_x$) to the atmosphere.

- Because the atmosphere is oxidizing, SO$_x$ and NO$_x$ → H$_2$SO$_4$ and HNO$_3$, which are strong acids.

→ Most H$_2$SO$_4$ is produced where fossil fuels contain high levels of sulfur
• High levels of HNO₃ are associated with high levels of human activity, since nitrogen oxides are produced by almost all combustion activities.

• Pure water in equilibrium with the atmosphere has pH = ?

• Aquatic critters are in trouble when pH < 5.5, and most are dead below pH = 5.

→ But lakes are buffered. This saves many lakes.
If you add acid, the H⁺ ions may be used up by a bicarbonate buffer:

\[ \text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \], \quad K_1 = 10^{-6.36} 

As long as there is a source of bicarbonate, then the lake can handle the addition of acid with only small changes in pH.

As soon as the bicarbonate is depleted, the pH drops precipitously . . .
Below ~pH 6.3, there is very little bicarbonate available.

A lake with a pH > 5.6 (due to carbonate buffering) must have an additional source of bicarbonate (soil or rock)
**FIGURE 5.24** Frequency histograms of fish status for 684 Norwegian lakes categorized as bicarbonate, transition, or acid lakes. (Wright, 1984)
If there is limestone, look what happens:

$$H^+ + CaCO_3 \rightarrow Ca^{2+} + HCO_3^-$$

$$HCO_3^- + H^+ \rightarrow H_2CO_3 \rightarrow CO_{2,g} + H_2O$$

This is a great thing for lakes but not so good for statues!

Lakes in granite areas are much more susceptible to acidification.

Limestone is added to many lakes.

The most vulnerable lakes are in granite areas with steep watersheds, thin soil, and conifers.
Ammonium ion concentration, 1997

Sites not pictured:
AK01   0.01 mg/L
AK03   0.05 mg/L

National Atmospheric Deposition Program/National Trends Network
http://nadp.sws.uiuc.edu
Ammonium ion concentration, 2007

Sites not pictured:
AK01 0.02 mg/L
AK03 0.01 mg/L
PR20 0.03 mg/L
VI01 0.03 mg/L

National Atmospheric Deposition Program/National Trends Network
http://nadp.sws.uiuc.edu
Nitrate ion concentration, 2007

Sites not pictured:
AK01 0.2 mg/L
AK03 0.1 mg/L
PR20 0.2 mg/L
VI01 0.3 mg/L

Nitrate as NO₃⁻ (mg/L)

- ≤ 0.60
- 0.60 - 0.75
- 0.75 - 0.90
- 0.90 - 1.05
- 1.05 - 1.20
- 1.20 - 1.35
- 1.35 - 1.50
- 1.50 - 1.65
- 1.65 - 1.80
- > 1.80

National Atmospheric Deposition Program/National Trends Network
http://nadp.sws.uiuc.edu
Sulfate ion concentration, 2007

Sites not pictured:
AK01  0.2 mg/L
AK03  0.2 mg/L
PR20  0.6 mg/L
VI01  0.8 mg/L

National Atmospheric Deposition Program/National Trends Network
http://nadp.sws.uiuc.edu
Magnesium ion concentration, 1997

Sites not pictured:
AK01        6 µg/L
AK03        5 µg/L

National Atmospheric Deposition Program/National Trends Network
http://nadp.sws.uiuc.edu
Calcium ion concentration, 1997

Sites not pictured:
AK01 0.03 mg/L
AK03 0.02 mg/L

National Atmospheric Deposition Program/National Trends Network
http://nadp.sws.uiuc.edu
Calcium ion concentration, 2007

Sites not pictured:
AK01 0.04 mg/L
AK03 0.02 mg/L
PR20 0.11 mg/L
VI01 0.12 mg/L

National Atmospheric Deposition Program/National Trends Network
http://nadp.sws.uiuc.edu
Hydrogen ion concentration as pH from measurements made at the Central Analytical Laboratory, 1997

Sites not pictured:
AK01  5.1
AK03  5.2

National Atmospheric Deposition Program/National Trends Network
http://nadp.sws.uiuc.edu
Hydrogen ion concentration as pH from measurements made at the Central Analytical Laboratory, 2002

Sites not pictured:
AK01  5.3
AK03  5.1
CA95   6.2
HI99   4.7
VIO1   4.8

National Atmospheric Deposition Program/National Trends Network
http://nadp.sws.uiuc.edu
Hydrogen ion concentration as pH from measurements made at the Central Analytical Laboratory, 2007

Sites not pictured:
AK01  5.1
AK03  5.3
PR20  5.2
VI01  5.0

National Atmospheric Deposition Program/National Trends Network
http://nadp.sws.uiuc.edu
Mobilization of Aluminum

• For pH < 5, a common result of acidification is the mobilization of aluminum from clay soils (similar process as limestone dissolution, but with the opposite effect):

\[
\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 6\text{H}^+ \rightarrow 2\text{Al}^{3+} + 2\text{Si(OH)}_4 + \text{H}_2\text{O}
\]

Clay Kaolinite

Unfortunately, Al\(^{3+}\) is very toxic to fish.