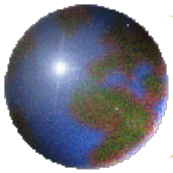
Environmental Chemistry

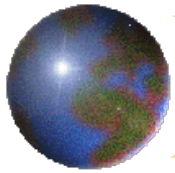


Topics

- Natural Cycles
  - Water
  - Oxygen
  - Carbon
  - Nitrogen
  - Energy
- Anthropogenic Burdens
- Enviromental Divisions
  - Atmosphere
  - Hydrosphere
  - Biosphere
  - Lithosphere
- *"Better Living through Chemistry"*

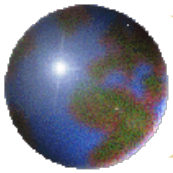
"Solution to Pollution is Dilution"

- Mantra presumes infinite reservoirs.
  - Treats pollution as a local concentration to be reduced by an ∞ of natural purity.
  - Need for reduction well below *LD50*.
  - Diffusion and mass transport aid the myth.
- Unrelenting contamination overwhelms.
  - All sinks are finite sinks.
  - Equilibrium and kinetics are unforgiving.



Kinetics and Thermodynamics

- In evolving systems, current states are a function of both.
  - Thermodynamics says where equilibrium would lie if it ever arrived.
  - Kinetics declares the rate at which species are evolving in time.
    - Via the rates of chemical reactions
    - Via diffusion and mass transport



Degradation in Dilution Model

- As equilibrium (pollution homogeneity) approaches, sink rates slow.
- Product "pressures" dictate that reverse reactions (return of contaminants) rise to counter the cleansing protocols.
- ∴ dilution is not the answer.
  - Understanding & long-range planning are.

Global Water Cycle

- Despite drought and its famine …
  - Water's global cycle is little altered by us.
  - Solar evaporation → humid atmosphere
  - Cresting waves → microscopic salt crystals
  - Rising air currents → lower air $T_{adiabatic}$
  - Salt crystals seed condensation.
  - Rainfall snares soluble gases, feeds Life, erodes mountains, and returns to the sea.

But, as everything is connected…

- Anthropogenic **particulates** influence *where* it rains, and downwind it doesn't.
- Anthropogenic combustion influences what the rain dissolves and bombards.
  - H_2O, the universal solvent, brings acid rain.
- Global Warming shifts precip. patterns.
  - Redistributes coastlines and grain belts.
  - Feast & famine migrates on the globe.

Acid Rain

- Natural Acidity, $CO_2(aq)$
  - P_{CO_2} = 370 ppmv, K_H, K_{a1} yield pH 5.6
- SO_3 & N_2O_5 are strong acid anhydrides.
  - Vulcanism, sour crude, and ore smelting produce $S☹_3$; Nature is a minority polluter.
  - $CaS☺_4$ & $H_2S☺_4$ recovery are economical.
- pH 4 recorded in (now dead) lakes.

O_2 Cycle Secure

- Atmospheric O_2 now at 1.2×10^{15} ton
  - Holding there for over 500 million years!
  - Biosphere holds only 10^{13} ton, but seas are a 1.4×10^{18} ton reserve (as H_2O).
- Photosynthesis/Decay are the major source/sink at 10^9 ton each *annually*.
  - 10^{15} ton/10^9 ton $yr^{-1} \approx 10^6$ yr O_2 lifetime
  - Unless we clearcut & poison seas, O_2 is OK.

Carbon Cycle

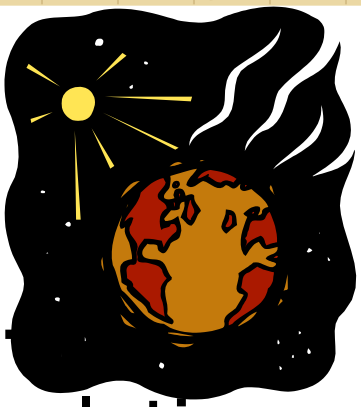
- Natural
  - 2.5×10^{12} ton in atmosphere vs. 1.3×10^{14} in sea.
    - 10^{11} ton yr^{-1} exchange gives ~25 yr residency.
    - So oceans are the perfect sink for excess CO_2.
  - 10^{13} ton in biosphere exchange 6×10^{10} ton yr^{-1}.
- Anthropogenic
  - Fuel burn at ~10% of photosynthesis/decay exchange increases atmospheric CO_2. Seas *can* absorb but only eventually. Le Châtlier wins.

Growing CO_2 Warms the Earth

- *Greenhouse Effect* is <u>essential</u> for Life!
  - Earth's radiative balance (solar input vs. IR output) leaves $\langle T_{Earth} \rangle \sim$ **– 20°C**
    - Almost all water would be ice everywhere.
    - But Life requires ℓiquid water!
  - $H_2O(g)$ and CO_2 absorb outbound IR and reradiate it **omni**directionally.
    - So Earth intercepts ~½ that absorbed IR and gains <T> to +15°C. ∴ $H_2O(\ell)$ & we exist.

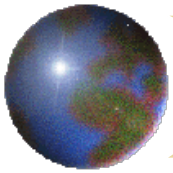
Venus, the Runaway Greenhouse

- Being closer to Sol, Venus intercepts twice the solar flux of Earth.
- But it is twice as reflective (*albedo*), so its $<T_{radiative}>$ is about the same, –29°C.
- But it's surface T averages **+435°C**!
- 90 atm CO_2 gives an IR *thickness* of 68.
  - Earth's optical thickness is only 0.68



Earthly Implications

- We won't become Venus, but …
- P_{CO2} up 30% since Industrial Revolution.
  - Fossil fuel combustion. P_{CO2} now 370 ppmv
- Growth in 2000 is **+0.4%** per year
  - 2× the average growth rate of last 150 yrs.
  - ~600 ppmv in next 75 yrs, over 2× natural.
  - Earth's <T> is rising. $\Delta T \sim 2\text{-}3°C$ now.
    - 5-6°C triggers climate changes.



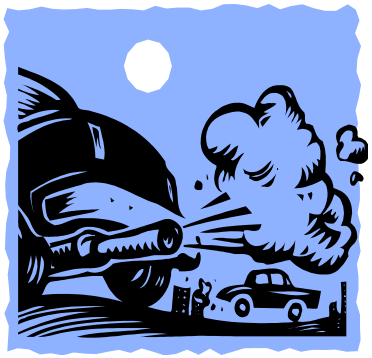
Greenhouse Fixes

- Negative population growth.
  - Guarantees standard of living but impractical.
- *Reduce burning* of fossil fuels & forests.
  - H_2/O_2 **fuel cells** work in developed countries.
  - Nuclear power grid practical but unpopular.
  - But developing countries cannot afford either and have the highest population growths!
- Plan for and resign to the changes.

Nitrogen Cycle

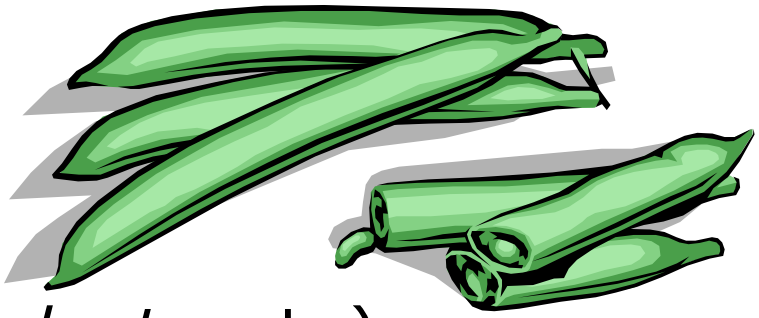
- Natural
  - 3.8×10^{15} ton in atmosphere resident 10^7 yrs.
  - Only 2.2×10^{13} ton in sea; 3.5×10^{10} in biomass
  - Life requires *fixation* (to NH_3) by bacteria.
    - 2.3×10^8 ton/yr *fixation* and (reverse) *denitrification*
- Anthropogenic
  - Crops, fertilizer & engines *fix* 0.8×10^8 ton/yr
  - Combustion denitrifies 0.3×10^8 ton/yr
  - Only a 13 ppb annual change; N☺ sweat.

Nitrogen Caveats

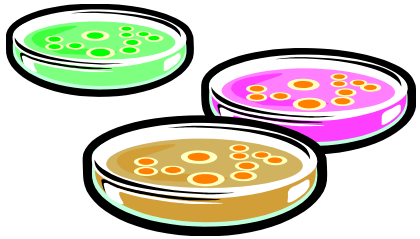


- NO_X (generic nitrogen oxides)
  - Fixation in engines generates NO_X
    - Terrestrial contaminant of acid rain (HNO_3)
    - Stratospheric contaminant of ozone destruction
      - $NO + O_3 \rightarrow NO_2 + O_2$
      - $NO_2 + O \rightarrow NO + O_2$
  - Runoff from fertilized fields
    - Supports algal growth in waterways.
    - Algae consume O_2 and suffocate water fauna.

The Chemistry



- Fixation (*Rhizobia, Azotobacter*, etc.)
  - $N_2 + 6e^- + 12ATP + 12H_2O \rightarrow 2NH_4^+ + 12ADP + 4H^+$
  - $N_2 + 3H_2 \rightarrow 2NH_3$ (Haber Process, 450°C, 200 atm, cat.)
- Nitrification (*Nitrobacter*)
  - $NH_3 + (3/2)O_2 \rightarrow NO_2^- + H_2O + H^+$



- Denitrification (*Pseudomonas*)
  - $2NO_3^+ + 12H^+ + 10e^- \rightarrow N_2 + 6H_2O$
    - Only runs under anaerobic conditions: wetlands & swamps
    - Those are disappearing with development.

The Energy Cycle

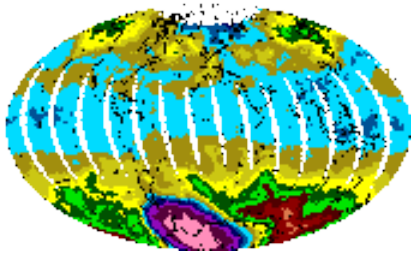
- 1/3 of available solar energy absorbed.
  - 2/3 (planetary *albedo*) reflected into space.
  - Most insolation warms oceans.
  - Oceanic gyres (currents) transport solar heat to the poles to disperse it (where insolation is oblique) returning cold water.
  - Earth's energy departs as infrared light.
- Man's heat budget no threat to Nature.
  - **<u>But</u> climate change & desertification change albedo!**

The Atmosphere

- A heated ideal gas w condensible (H_2O)
  - $\therefore$ turbulent in the majority of its moles.
- Mesosphere interacts w solar *"wind."*
    - $O_2 + h\nu_{UVC} \rightarrow 2\ O \quad \lambda < 2000\text{Å}$
- Stratosphere, home to the O_3 blanket.
  - $O + O_2 + M \rightarrow O_3 + M^*$
  - $O_3 + h\nu_{UVB} \rightarrow O + O_2 + \text{heat} \quad \lambda < 3000\text{Å}$
    - $O + O_3 \rightarrow 2\ O_2$

Stratospheric Contamination

- CFC, chlorofluorocarbons ($C_nCl_xF_y$)
  - $CF_yCl_x + h\nu_{UV} \rightarrow CF_yCl_{x-1} + Cl$
  - $Cl + O_3 \rightarrow ClO + O_2$
  - $ClO + O \rightarrow Cl + O_2$
    - ~50 year ClO_X lifetime & still migrating up.
    - Ozone hole at both poles migrating down.
    - NO_X also destroys odd oxygen catalytically.

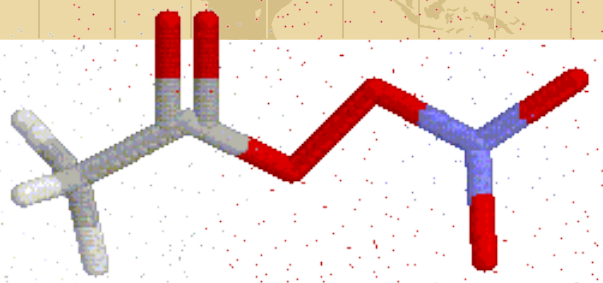


- Fix: international agreement to end CFC

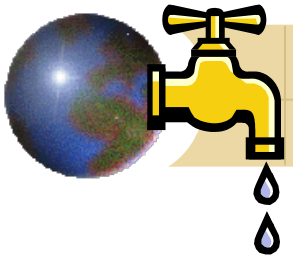
Troposphere

- Up to 8-12 km above sea level.
  - Turbulent!
  - Tropopause (boundary with stratosphere) stops weather because it's warmer above.
- Air pollution in troposphere (photochemistry)
  - $NO_2 + O_2 + h\nu \rightarrow NO + O_3$
  - $O_3 + h\nu \rightarrow O + O_2$
  - $O + H_2O \rightarrow 2\ \mathbf{OH}$ [OH] ~ 10^6 molecules/cc
  - OH radical is dominant oxidizer in troposphere!

Smog: health hazard



- "Smoke and fog," a term from London.
- Engine exhaust components
  - CO, NO, unburnt hydrocarbons
  - Lean mix minimizes CO, hc, maximizes NO
  - Rich mix minimizes NO, maximizes CO, hc
    - Run a little rich and catalytically kill CO to CO_2
  - $OH + CO + O_2 \rightarrow CO_2 + HO_2$
  - Peroxides like **P**eroxy**A**cetyl**N**itrate result



Hydrosphere

- All the waterways on Earth
  - Civilization created on rivers (Euphrates)
- Population pressure
  - Irrigation consumes rivers, lakes, aquifers
  - Salts concentrated in what little is left
- Industrial and Agricultural pollution
  - Both chemical and thermal (remediable)

Biosphere

- The zone of Life
  - Wherever it's found: thermal vents?
- Ocean: Life's Nursery and O_2 Factory
  - Phytoplankton make ~90% of photo-synthetic O_2 on Earth. *Sensitive to UV!*
  - So bigger ozone holes adversely effect O_2 production.
  - Phytoplankton→Zooplankton→Fish→Us.

Frankenfixes

- Altering the environment chemically alters the kind and number of lifeforms.
- Cleaning the environment can rest, in part, on genetic engineering.
  - Giving wheat *Rhizobia,* reduces fertilizer.
  - Giving bacteria a taste for oil, cleans spills.
  - But it's not nice to fool Mother Nature unless you are as smart as She.

Environmental Awareness

- As scientists, we are morally obliged to consider the consequences of our acts.
- We create a molecule for profit but must consider its fate when discarded.
  - E.g., plastic bottles now biodegrade and are no longer immortal.
  - E.g., non-chlorinated refrigerants now cool beer without sacrificing the Ozone Layer.