The Carbon Cycle

- Consider the oxidation states of carbon.
  - The range of oxidation states is determined by the ground state electronic configuration of the C atom, $1s^2 2s^2 2p^2$.
  - Carbon must either gain four electrons or lose four electrons to have a closed shell configuration.
  - Range of oxidation states is therefore +4 to -4.
- Some examples of oxidation state of carbon:
  - CO_2 is in oxidation state +4.
  - CO is in oxidation state +2.
  - HCO is in oxidation state +1.
  - H_2CO, C(graphite), C(diamond) are in oxidation state 0.
  - C_2H_2 is in oxidation state -1.
  - C_2H_4 is oxidation state -2.
  - CH_3 is in oxidation state -3.
  - CH_4 is in oxidation state -4.

- Carbon fixation puts carbon into biologically available forms.
  - Photosynthesis uses 8 photons to drive the reaction:

$$6CO_2 \ + \ 6H_2O \rightarrow \ C_6H_{12}O_6 \ + \ 6O_2$$

  which requires 2801.3 kJ per mole of glucose (467 kJ per mole of carbon).
- Photosynthesis is coupled to the energy cycle by the phosphorous cycle.
- The CO_2 cycle is coupled to the hydrologic and energy cycle.
  - Before 1800, the level of atmospheric CO_2 was about 280 ppm.
  - The 1800's saw the beginning of the industrial revolution and increased use of fossil fuel.
  - In 1994, atmospheric CO_2 was observed to be 358 ppm.
- The global budget of CO_2 has not been fully determined.

$$\mathrm{CO_2(atmospheric) + H_2O \rightarrow solubilized\ speciated\ C(IV)}$$

$$\mathrm{CO_2(g) \rightleftharpoons CO_2(aq)}$$

$$\mathrm{CO_2(aq) + H_2O \rightleftharpoons H_2CO_3(aq)}$$

$$\mathrm{H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq)}$$

$$\mathrm{HCO_3^- \rightleftharpoons CO_3^{2-} + H^+}$$

  - CO_3^{2-} precipitates and is incorporated into shells of aquatic animals such as coral.
- Organic carbon comprises oxidation states 0 to -4.
  - Living organic carbon may be represented as $\{CH_2O\}$
  - Fossil organic carbon is reduced and may be represented as $(CH_2)_nH_2$ and is produced by biogeochemical processes.
- Reservoirs of organic carbon include:

  - Oceans with 5.8 × 10^{14} moles of carbon in biomass, 5 × 10^{15} moles C as suspended $\{CH_2O\}$ particles, 5.8 × 10^{16} moles C as dissolved organic carbon.
  - By comparison, oceans contain 3.2 × 10^{18} moles of C as C(IV).
  - On land, 4 × 10^{16} moles C is found in living biomass with a residence time of 16 years.

  - On land, living and dead biomass combined account for 1 × 10^{17} moles of C with a residence time of 40 years.
- The atmosphere provides a reservoir for a number of carbon containing species.

ppm	Species	mol C	τ
1.7	CH_4	5.2 × 10^{14}	3.6 yrs
0.1	CO	1.9 × 10^{13}	0.1 yr
360	CO_2	5 × 10^{16}	4 yr

  - In addition the atmosphere contains smog (smoky fog) and carbon containing particulates (such as soot) which account for 2.9 × 10^{14} mol of C.
  - The atmospheric reservoirs are coupled to the biomass cycle.
- Recent sediments under the ocean are also significant reservoirs for carbon.
  - 50.8 ×10^{20} mol of C as CO_3^{2-}
  - 10.4 ×10^{20} mol of C as $\{CH_2O\}$
  - Both of these have a lifetime 342 years.
- Sources for recent sediments are in the form of:
  - 6.1 × 10^{12} mol C yr^{-1} as $\{CH_2O\}$
  - 11.8 × 10^{12} mol C yr^{-1} as CO_3^{2-}
- Sinks for recent sediments consist of transfer to old sediments (burial):
  - 2.5 × 10^{12} mol C yr^{-1} as $\{CH_2O\}$
  - 15.4 × 10^{12} mol C yr^{-1} as CO_3^{2-} in the form of $CaCO_3$ and $MgCO_3$
  - These sinks are balanced by transfer from old to recent sediments.
- Anthropogenic activity extracts 3.88 × 10^{12} mol C yr^{-1} as fossil fuel.
  - This is a net loss.

Nitrogen Cycle

- Consider the oxidation states of nitrogen.
  - The range of oxidation states is determined by the ground state electronic configuration of the N atom, $1s^2 2s^2 2p^3$.
  - Nitrogen must either gain three electrons or lose five electrons to have a closed shell configuration.
  - Range of oxidation states is therefore +5 to -3.
- Some examples of oxidation state of nitrogen:
  - NO_3^- and N_2O_5 are in oxidation state +5.

  - NO_2 is in oxidation state +4.
  - N_2 is in oxidation state 0.
  - NH_3 and NH_4^+ are in oxidation state -3.
- Nitrogen is essential to amino acids.
- The atmosphere is the main reservoir of nitrogen:
  - Contains 3.9×10^{18} N
  - 78% of the atmosphere
  - $\tau \sim 10^7$ years
- In order to be biologically available, N must be fixed.
  - 2×10^{11} kg N fixed a year.
  - Anthropogenic fixation accounts for 5×10^{10} kg N y^{-1}.

- Biological fixation of nitrogen is coupled to the carbon cycle.

$$3\ \{CH_2O\} + 2\ N_2 + 3\ H_2O + 4\ H^+ \rightarrow 3\ CO_2 + 4\ NH_4^+$$

  - If the pH is sufficiently high, NH_3 is released.
- Fixation of nitrogen may be considered from a redox perspective:

$$N_2 + 8H^+ + 6e^- \rightarrow 2NH_4^+$$
$$\{CH_2O\} + H_2O \rightarrow CO_2 + 4e^-$$

- Biological fixation occurs with
  - Aquatic organism such as Azobacter, Clostridium, and Cyanobacter (formerly known as bluegreen algae).
  - Terrestial organism Rhizobium in symbiosis with legumes (peas, beans, peanuts). The Rhizobium infect root hairs to draw on the legumes organic carbon from photosynthesis.
- Not enough nitrogen is fixed annually to satisfy the current biomass requirements.
- Anthropogenic fixation occurs by the Haber Process:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

  - The process is catalyzed by Fe, K_2O, and Al_2O_3
  - The process is endothermic with $\Delta H = 92.6$ kJ mol^{-1} N_2.
  - Used to form NH_4NO_3 for fertilizer and explosives.
- Organically bound N occurs in humus ($N/C \approx 1/10$) and can be released on a time scale similar to that of plant growth.
- Nitrification is the process of transforming N(-3) to N(+5):
  - From a redox perspective:

$$NH_4^+ + 3\ H_2O \rightarrow NO_3^- + 10\ H^+ + 8\ e^-$$
$$4\ H^+ + 4\ e^- + O_2 \rightarrow 2\ H_2O$$

$$NH_4^+ + 2\ O_2 \rightarrow NO_3^- + H_2O + 2\ H^+$$

  - Nitrification is a thermodynamically favoured process with $K = 10^{60.72} = 5.25 \times 10^{60}$.
- NO_3^- may be absorbed by plants.

- Nitrification can occurs naturally as a two step process mediated by bacteria:
  - $NH_4^+ \rightarrow NO_2^-$ is mediated by nitrosomonas.
  - $NO_2^- \rightarrow NO_3^-$ is mediated by nitrobacter.
  - Both are obligate aerobes that require O_2 for the oxidation process.
  - This is why aeration of soil is important.
- NO_3^- may act as an oxygen source for anaerobes.
  - Do not want nitrification to occur during sewage treatment because of subsequent denitrification.
- Thunderstorms may contribute to the production of NO_3^-.

$$N_2 + O_2 \rightarrow 2NO$$
$$NO \rightarrow \cdots \rightarrow HNO_3$$

  - HNO_3 is scavenged efficiently by cloud droplets.
- Decay of biomass leads to the mineralization of nitrogen in the form of NO_2^- and NO_3^-.
- Denitrification is the removal of nitrogen from the biologically available forms.
  - Returns N_2 to the atmosphere.
  - Involves the reduction of NO_3^- and the oxidation of NH_3.

- Reduction of NO_3^- produces N_2O and NO, both of which are greenhouse gases.
- If reduction of NO_3^- occurs during sewage treatment, it is undesirable.
- Denitrification can also occur during sewage treatment:

$$4\ NO_3^- + 24\ H^+ + 20\ e^- \rightarrow 2\ N_2 + 12\ H_2O$$
$$5\ \{CH_2O\} + 5\ H_2O \rightarrow 5\ CO_2 + 20\ H^+ + 20\ e^-$$
$$4\ NO_3^- + 5\ \{CH_2O\} + 4\ H^+ \rightarrow 2\ N_2 + 5\ CO_2 + 7\ H_2O$$

  - N_2 and CO_2 bubbles are formed and prevent settling.

Phosphorous Cycle

- Consider the oxidation states of phosphorous.
  - The range of oxidation states is determined by the ground state electronic configuration of the P atom, $1s^2 2s^2 2p^6 3s^2 3p^3$.
  - Phosphorous must either gain three electrons or lose five electrons to have a closed shell configuration.
  - $3d$ orbitals available for contribution expanded octet configurations.

  - Range of oxidation states is therefore +5 to -3.
- Some examples of oxidation state of phosphorous:
  - PH_3 is in oxidation state +3
  - PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, H_3PO_4 and associated polyphosphates are in oxidation state +5.
- In many cases, P is the limiting element in biological uptake.
  - C:N:P are taken up in the ratio 100:15:1
  - P is essential to ADP and ATP in organisms.

- The primary reservoir is the geosphere as various forms of phosphate.
  - There is no gas phase reservoir for P.
  - The solubilty of phosphates is strongly pH dependent.
- Phosphates in the geosphere include insoluble mineral forms of phosphate:
  - Hydroxyapatite is very insoluble ($K_{sp} = 10^{-59}$ M^9)
    $$Ca_5(PO_4)_3OH \rightleftharpoons 5\ Ca^{2+} + 3\ PO_4^{-3} + OH^-$$
  - Hydroxyapatite is also found in tooth enamel.
- Occluded phosphorous is not biologically available.
  - Soil contains Fe_2O_3 and Al_2O_3 and aluminosilicates.
  - The associated hydrates form an amorphous matrix, with orthophosphate (monophosphate) contained within the matrix.
- Non-occluded phosphorous is primarily in the form of orthophosphate bound to surface silicate (SiO_2) or $CaCO_3$.
  - Depending on pH, this is more soluble than occluded phosphorous
- Anthropogenic environmental impact of phosphorous compounds is of most concern in aquatic reservoirs.
  - Soluble forms of phosphate include orthophosphate, linear polyphosphate ($P_3O_{10}^{5-}$) and cyclic polyphosphates ($P_3O_9^{3-}$)
- Solubility of phosphates are closely connected to their speciation.
  - Consider rock phosphate, $Ca_3(PO_4)_2$, which has a $K_{sp} = 10^{-24}$ M^5
    $$Ca_3(PO_4)_2 \rightleftharpoons 3\ Ca^{2+} + 2\ PO_4^{2-}$$
  - This equilibrates with HPO_4^{2-} and $H_2PO_4^-$ in according with pH, the above K_{sp} and K_{a1}, K_{a2}, and K_{a3}.
    $$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+;\ K_{a1} = 7.5 \times 10^{-3}\ M$$
    $$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+;\ K_{a2} = 6.2 \times 10^{-8}\ M$$
    $$HPO_4^- \rightleftharpoons PO_4^{3-} + H^+;\ K_{a3} = 4.8 \times 10^{-13}\ M$$
  - Solubility of $CaHPO_4$ and $Ca(H_2PO_4)_2$ can be calculated from the above reactions.
  - It is the protonated forms that are effective for biological uptake.
  - Phosphate for fertilizer is prepared by mixing sulphuric acid with rock phosphate.
- Anthropogenic impact on P levels is due to:
  - Phosphate fertilizers
  - sewage
  - detergents
- Phosphate in detergents was primarily in the form of sodium tripolyphosphate or STP, $Na_3H_2P_3O_{10}$.
  - STP was added as a “builder”, or a source of hydroxide ion, but does not precipitate Ca^{2+}
  - This keeps the pH high enough that the detergent molecules are in their ionic form.
  - The ionic form of a detergent or soap is active as a surfactant.
  - In addition to detergent (or soap) and a builder, laundry detergent products may contain bleach, zeolites, non-ionic surfactants, and bluing or brightening agents.

  - Use of STP in detergents has been restricted since the late 1970's. In Canada and Europe the sodium salt of nitrilotriacetic acid (NTA) is used as a builder instead of STP.
- Discharge of phosphates can lead to algal blooms in lakes and can promote eutrophication.
  - Treatment of sewage removes phosphates by precipitation with Ca^{2+} at high pH.
- Biologically, phosphate is found in:
  - Nucleic acids
  - ADP/ATP
  - bones and teeth
- Phosphorothionate and phosophorodithionate pesticides do not bioaccumulate.

Oxygen Cycle

- Electronic configuration of oxygen is $1s^2 2s^2 2p^4$.
  - Oxidation states are 0,-1, and -2.
- Some examples of oxidation states of oxygen are:
  - Oxidation state 0: O_2
  - Oxidation state -1: OH radical, peroxides HOOH, ROOH.
  - Oxidation state -2: H_2O, oxides, and organic compounds.
- Coupled to the energy cycle and the carbon cycle by photosynthesis.
  - All atmospheric O_2 comes from photosynthesis.
- Primary reservoir is the atmosphere.
  - O, O_2, and O_3 are involved in the Chapman Cycle and are found in the mesosphere, stratosphere, and troposphere.
- Many oxygen containing species in the atmosphere.
  - Nitrogen oxide species NO_x and NO_y include NO, NO_2, NO_3, and N_2O.
  - Sulphur containing species SO_x refers to SO_2 which can be further oxidized.
  - Hydrogen containing species HO_x refers to OH and HO_2, which are important free radicals in atmospheric chemistry.
  - Oxygen is also found in atmospheric organic compounds, known as VOCs or volatile organic carbon
- Sinks for oxygen include weathering and the formation of metal oxides.
  - These processes are exothermic and spontaneous.
  - In constrast, the smelting of metals (reducing the oxide to the pure metal) is endothermic.
- Properties and reactivity of atmospheric oxygen have their origins in the electronic structure with unpaired electrons in both the atom and diatom.
  - Two common electronic states of the atom are the ground state (^{3}P) and the excited state (^{1}D).
  - Two common electronic states of the molecule are the ground state ($^3\Pi$) and the excited state ($^1\Delta$).
  - The main source of atmospheric OH is:

$$O(^1D) + H_2O \rightarrow 2OH$$

  - The source of O(^{1}D) is the photolysis of ozone:

$$O_3 + h\nu \rightarrow O(^1D) + O_2(^1\Delta)$$

  - Ozone also photolyzes to the ground states:

$$O_3 + h\nu \rightarrow O(^3P) + O_2(^3\Pi)$$

  - Photons of wavelength 310 nm or shorter required.

Sulphur Cycle

- Electronic configuration of sulphur is $1s^2 2s^2 2p^6 3s^2 3p^4$.
  - Oxidation states range from +6 to -2.
- Some examples of the oxidation states of sulphur:
  - SO_3, H_2SO_4, HSO_4^-, and SO_4^{2-} are in oxidation state +6.
  - SO_2, H_2SO_3, HSO_3^-, and SO_3^{2-} are in oxidation state +4.
  - S_8 is in oxidation state 0.
  - S_2^{2-} and FeS_2 (pyrite) are in oxidation state -1.
  - H_2S and Fe_2S_3 contain S in oxidation state -2.
- The S cycle is coupled to the O cycle.
- The geosphere is an important reservoir with S found in:
  - Sulphate salts
  - Sulphite salts
  - metal disulfide ores
  - metal sulphide ores.
  - Since proteins contain S, fossil fuels will contain S.
- Anthropogenic impacts are most significant in the atmospheric reservoir.
- Atmospheric species include:
  - Sulphur dioxide, SO_2
  - Dimethyl sulphide or DMS, CH_3SCH_3
  - Dimethyl disulphide or DMDS, CH_3SSCH_3
  - Carbonyl sulphide or OCS, O=C=S
  - Carbon disulphide, S=C=S
  - Hydrogen sulphide or (H_2S)
- Anthropogenic emissions are three times natural emissions.
  - Most anthropogenic emissions are as SO_2 from smelting of metals and combustion of fossil fuels.
  - In contrast, most natural emissions are reduced forms of sulphur since anaerobic organisms use S(VI) as a source of oxygen.
  - Natural emissions include DMS, CS_2, and OCS from the reduction of amino acids.
  - With the exception of OCS, the reduced species can be oxidized in the troposphere.
  - OCS is transported to the stratosphere where it is photolyzed.
- Volcanic emissions include SO_2, H_2S, and OCS.

  - May be injected directly into the stratosphere.
- Atmospheric oxidation of H_2S proceeds by the sequence:

$$H_2S + OH \rightarrow HS + H_2O$$
$$HS + O_2 \rightarrow OH + SO$$
$$SO + O_2 \rightarrow SO_2 + O$$

- Atmospheric oxidation of SO_2 proceeds by several routes.
  - Direct gas phase oxidation is too slow to be significant.

$$SO_2 + O_2 \rightarrow SO_3 + O$$

  - Gas phase oxidation can occur with photochemical oxidants formed in photochemical smog by nonmethane hydrocarbons (NMHC). These oxidants includes OH, HO_2, O, O_3, NO_3, N_2O_5, ROO, and RO.
- Aqueous phase oxidation inside cloud droplets is the dominant route.
  - SO_2 is effectively scavenged by cloud droplets as are oxidants such as O_2, O_3, HO, H_2O_2, ROOH, CH_3OOH, and $CH_3(CO)OOH$ (peroxyacetic acid or PAA).
  - Aqueous phase oxidation with O_2 is catalyzed by Fe^{2+}, Mn^{2+} and C.
  - Aqueous phase oxidation with O_3, OH, and H_2O_2 is pH sensitive and is connected with the S(IV) speciation. HSO_3^- is more easily oxidized than other species of S(IV).
- A major anthropogenic source of SO_2 is the roasting of metal ores. For example:

$$NiS + \tfrac{3}{2}O_2 \rightarrow NiO + SO_2$$

Water Treatment

- It is desired that drinking water be:
  - Safe
  - Clean
  - Clear
  - Free of disagreeable smells and odours
  - Free of pathogens (Over 7000 people a day die due to waterborne diseases that could be prevented with water treatment.)
  - Free of dissolved solids or minerals
  - Conveniently and inexpensively available.
- Sources of drinking water:
  - Ground water
  - Surface water
- The advantages of ground water include:
  - Fewer contaminants (usually)
  - Clarity
- Disadvantages of ground water include:
  - Radon

  - Hardness and alkalinity

  - Finite capacity of aquifers. If an aquifer is depleted, the ground above may subside and become vulnerable to flooding.
- The advantages of surface water include:
  - Availability
- Disadvantages of surface water include:
  - What is upstream?
  - Dissolved organic matter.
  - Biological and chemical oxygen demand.
- Since it was recognized that ground water was better than surface water, the first attempts at water treatment in the 19th century was to "make" ground water.
  - Surface water was trickled through sand.
  - Surface water was used to "reinject" underwater aquifers.
  - This does lead to a decline in the incidence of waterborne diseases such as cholera, typhoid, and amoebic dysentery.
- Modern water treatment consists (typically) of four stages:
  - Settling
  - Aeration
  - Coagulation
  - Disinfection
- Depending on the water supply, one or more of the first three steps may not be necessary.

Settling

- Water brought into a large holding pond an particulate is allowed to settle.
- If the pH is too low, it is adjusted to be greater than 6.5

Aeration

- Aeration has the objective of removing oxidizable substances.
  - These include be both chemical and biological species.
  - Fe^{2+} is removed at this stage to prevent rust stains ($Fe(OH)_3$).
  - Upon contact with air Fe^{2+} is quickly oxidized to Fe^{3+}.

$$Fe^{2+} \rightarrow Fe^{3+} + e^-$$

$$4\ H^+ + O_2 + 4\ e^- \rightarrow 2\ H_2O$$

$$\text{Net reaction: } 4\ Fe^2 + +4\ H^+ + O_2 \rightarrow 4\ Fe^3 + 2\ H_2O$$

  - If $pH > 3$,then:

$$Fe^{3+} + 3\ OH^- \rightarrow Fe(OH)_3$$

Coagulation (Secondary Settling)

- Coagulation has the objective of removing suspended solids such as:
  - Colloidal minerals
  - Bacteria
  - Pollen

  - Spores

  resulting in water that is clear.

- Since in the settling step, the pH of the water has been adjusted to pH > 6.5.
  - Minimum solubility of Al^3+ occurs in the pH range 6.5 to 8.
  - Filter alum ($Al_2(SO_4)_3.18H_2O$) is used as a clarifying agent since it forms a gelatinous precipitate that settles slowly, carrying down the suspended solids.
  - Alternative settling agents are $Fe(OH)_3$ and activated silica, both of which form gelatinous precipitates.

Disinfection

- Disinfection of drinking water is essential
  - To kill any pathogens that persist through the earlier stages of treatment.
  - To prevent the growth of bacteria in the distribution system (in which water can spend up to a week).
  - To prevent recontamination of the water in the distribution system due to leaks.
- Disinfection agents include:
  - Chlorine
  - Chlorine Dioxide
  - Ozone
  - Ultraviolet radiation
- Chlorine is the only one that leave a residual that can prevent recontamination.
- Chlorine dissolved in water establishes the following equilibria:

$$\begin{aligned}
&\mathrm{Cl_2(g)} \rightleftharpoons \mathrm{Cl_2(aq)}, \quad K_H = 8.0 \times 10^{-3}\ \mathrm{mol\ L^{-1}\ atm^{-1}} \\
&\mathrm{Cl_2(aq)} + \mathrm{H_2O(l)} \rightleftharpoons \mathrm{H^+(aq)} + \mathrm{Cl^-(aq)} + \mathrm{HOCl(aq)} \\
&\qquad\qquad K_c = 4.5 \times 10^{-4}\ \mathrm{mol^2\ L^{-2}} \\
&\mathrm{HOCl(aq)} \rightleftharpoons \mathrm{H^+(aq)} + \mathrm{OCl^-(aq)} \\
&\qquad\qquad K_c = 3.0 \times 10^{-8}\ \mathrm{mol\ L^{-1}}
\end{aligned}$$

  - It is HOCl that is effective in killing microorganisms since it can penetrate the cell membrane.
  - Chlorine dose required depends on pH (need to keep pH below 2.5).
  - Desire chlorine residual of about 1 ppm.
- Disadvantages of chlorine include:
  - Taste and odour.
  - Chlorination of organic compounds.
  - Concerns about toxicity.
- Advantages of chlorine include:
  - Inexpensive
  - Residual

- Chlorine dioxide is often considered as an alternative to chlorine.
- Chlorine dioxide has the advantages:

  - Oxidizes organic compounds instead of chlorinating them.
  - Can use a physical plant very similar to that required for chlorine.
  - Possible to easily switch from chlorine temporarily if chlorine is causing problems.
- Disadvantages of chlorine dioxide include:
  - Must be manufactured on site from $NaClO_2$.

$$\begin{gathered} 10\ \mathrm{NaClO_2} + 5\ \mathrm{H_2SO_4} \rightarrow \\ 8\ \mathrm{ClO_2} + 5\ \mathrm{Na_2SO_4} + 2\ \mathrm{HCl} + 4\ \mathrm{H_2O} \end{gathered}$$

or

$$\begin{gathered} 2\ \mathrm{NaClO_2} + \mathrm{Cl_2} \rightarrow 2\ \mathrm{ClO_2} + 2\ \mathrm{NaCl} \\ (\text{Must keep pH} < 3.5) \end{gathered}$$

  - The first reaction is preferred because it is chlorine free.
  - There is no residual disinfection, therefore the water must be “finished” with chlorine before distribution.
- There is some concerned about toxicity of ClO_2.
  - At levels of 50 ppm $NaClO_2$, hemolysis can occur.
  - Finished water has less than 1 ppm ClO_2, which is shortlived.

- Ozone requires a completely different physical infrastructure than chlorine or chlorine dioxide.
  - Usually implemented in new facilities.
  - Economic only on a larger scale.
  - Generated by running a high voltage electrical discharge through air giving about 1
  - Ozone absorbed by water ($K_H = 1.3 \times 10^{-2}$ mol L^{-1} atm^{-1}.)
- Advantages of ozone include:
  - Oxidizes organics
  - Air is the main raw material required.
- Disadvantages include:
  - pH control is necessary.
  - Finishing with chlorine is necessary.

- Ultraviolet radiation with $\lambda < 300$ nm damages pyridine base pairs in DNA sequences.
  - Causes cell death and thus death of microbes.
- Can be generated by mercury arc lamps ($\lambda = 254$ nm) with about 40% efficiency.
- Advantages of UV water treatment include:
  - Contact time is short (< 10 s).
  - No large reservoir required.
  - Low installation cost.
  - Do not need to control or monitor pH or temperature.
  - No toxic residues.
  - Cost competitive with chlorine treatment.
  - Possible to implement on a small or portable scale as an emergency or remote, stand alone system.

- Disadvantages of UV treatment include:
    - Water source must be clear of suspended matter and organic molecules that could absorb the UV.
    - If suspended matter or organic molecules are present, then pretreatment with activated charcoal may be required.
    - No residual disinfection. The water must be used immediately or be finished with chlorine.

Quality Control in Water Treatment and Distribution

- Before water treatment:
    - What are the potential contaminants in the watershed or aquifer?
    - What dissolved inorganic species are present?
    - What organic chemical species are present, especially those that can survive the treatment process and lead to unacceptable taste or smell?
    - For treatment with chlorine, chlorine dioxide, or ozone: what is the demand of the raw water for the disinfecting agent.
    - For treatment with UV, is the clarity acceptable.
    - Is the quality of the incoming water consistent with the capacity of the treatment facility.
- During water treatment:
    - Are the pH and temperature in the appropriate range for the treatment process?
- After water treatment:
    - Is there an appropriate level of residual chlorine?
    - Are any pathogens present?
    - Are there any undesirable chemicals present that formed during the treatment process or survived the treatment process?
    - Is further treatment (softening, deionization, filtering) required.
    - Are the taste, smell, and appearance acceptable.

Sewage Treatment

- Sewage treatment parallels water treatment.
    - Primary treatment consists of settling and skimming
    - Secondary treatment consists of reducing the biological oxygen demand.
    - Tertiary treatment reduces the concentration of particular contaminants, such as phosphorous.
    - Finishing consists of disinfection.
- Primary sewage treatment
    - Physical separation of solids and immiscibles.
    - Raw sewage enters a lagoon through one or more coarse screens that remove large objects.
    - A grit tank allows for the deposition of grit, sand, etc.
    - The sewage then moves slowly through the clarifier slowly enough for solids to settle.

  - At the same time, greasy material is skimmed off.
  - The result of primary treatment is clear effluent with a very high biological oxygen demand.
  - Solids removed are landfilled.
  - Some facilities use coagulating agents such as alum to aid the settling in the lagoon. This can reduce the BOD to the point that secondary treatment may not be necessary.
- Secondary treatment
  - Reduction of biological oxygen demand by at least 90%.
  - Usually done with either a trickling filter or an activated sludge reactor.
  - A trickling filter is a bed of sand of graduated particle size, ranging from coarse gravel on top to very fine sand on the bottom.
  - The trickling filter is colonized with microbes which reduce the BOD by utilizing the carbon compounds found in the sewage.
  - The activated sludge reactor is more compact and can be enclosed in climates too cold for optimum biological activity.
  - The reactor is a large tank in which the waste water is aerated to provide sufficient oxygen for the biological removal of BOD.
  - Microbial sludge leaving the reactor is reinjected to maintain colonization of microbes.
  - Many issues involved in the disposal of sewage sludge.
- Tertiary treatment is usually focused on the removal of phosphorous.
  - Usually achieved by precipitation with lime (a source of Ca^{2+}) or Al^{3+} or Fe^{3+}. The latter two form gelatinous precipitates which can further remove any microorganisms left from secondary treatment.
- Finishing usually involves a heavy dose of chlorine to kill remaining pathogens.
  - There is concern about chlorination of organics.

Sewage Sludge

- By-product of sewage treatment
  - High water content ($\sim 95\%$)
  - Difficult to handle
  - Needs to be digested to facilitate coagulation and dewatering.
  - Digestion of sludge produces methane, which can be used for co-generation of electricity or heat.
  - Dewatered sludge must be disposed of.
- Disposal of sludge may be by:
  - Landfilling
  - Incineration
  - Ocean dumping
  - Using as fertilizer.
- In using sewage sludge as fertilizer, there are a number of considerations.
  - High organic content with nitrogen and phosphorous can restore nutrients to soil in disturbed sites.

    - Allows soils to retain water.
    - Inexpensive alternative to other methods of disposal.
    - Sludge is low in nutrients compared to conventional fertilizers, so cost of handling and shipping must be kept low. In practice, this means that only local use in practical.
- Sludge may contain toxic substances.
    - Both organic and inorganic toxins can survive sewage treatment.
    - Oxidation resistant organics such as organochlorine compounds.
    - Inorganics such as As, Cd, Pb, Hg, and Zn, which usually have industrial sources.
    - Pathogens
    - Toxins may be taken up by vegetation, therefore most jurisdictions have strict limits on the use of sludge on agricultural lands.
    - Transfer of pathogens avoided by waiting periods between application of sludge and harvest.
    - Some metals are not harmful to human health, but can harm ruminants. (Cu is toxic to sheep.
- Fate of metal from sludge depends on properties of the soil.
    - Porous, gravelly soils allow transport of dissolved metals to watershed.
    - High organic muck soils facilitate biological uptake.
    - Clay soils have ion exchange properties and bind metal ions tightly, greatly reducing their mobility.
    - pH affects speciation, solubility, biological uptake, and binding to clay.

Tertiary Sewage Treatment

- Focused on one or more specific elements in the sewage, including P.
    - P is usually the limiting element in biological systems.
- P in sewage.
    - P can usually give rise to eutrophication.
    - Anthropogenic sources include fertilizer and detergent.
    - Phosphates removed by precipitation with Ca^{2+}, Al^{3+}, and Fe^{3+}.
- Tertiary treatment can also be used to further reduce BOD
    - Secondary treatment leaves a BOD of about 50 ppm O_2.
    - This is usually in the form of suspended organic matter.
    - May be removed by microstraining or coagulation.
    - Very fine (μm) stainless steel screens are used for microstraining.
    - Filter alum is used for coagulation and has the advantage of simultaneously reducing phosphate.
    - Tertiary BOD reduction is desirable so that high doses of chlorine are not required for disinfection.

- Tertiary treatment may include disinfection with chlorine
    - High doses of chlorine can lead to undesirable reactions between NH_3 and Cl_2 and between organic compounds and chlorine.
    - Production of chlorinated organics also an issue.

Other Aqueous Wastes

- The nature of the waste depends on the nature of the source.
    - Food processing
    - Pulp and paper
    - Metal finishing
    - Chemical manufacturing
    - Petroleum refining
    - Mining
    - Agriculture
    - Landfills

High Strength Aqueous Waste

- Very high BOD
- Come primarily from food processing and pulp and paper
- Contain naturally occurring organic compounds.
- If discharged into sewage system, can overwhelm the capacity of the sewage treatment facility.
    - Treatment required before discharge.
    - If municipalities allow discharge into sewage system, a commensurate levy is charged.
- Pulp and paper waste is primarily lignin.
    - Treated by biological degradation in vigorously aerated lagoons.
    - Alternative treatment involves closed bioreactors (which is less vulnerable to weather variation).
    - Resulting sludge needs to be digested, dewatered, and landfilled.

Low Strength Aqueous Waste

- Oily wastes generated by petroleum refining.
    - Interfere with oxygen transport across surface of water.
    - Broken down by long treatment in aeration lagoons or bioreactors.
    - Mechanical separation is difficult, especially if emulsifiers are present.
    - Water may be removed by evaporation.
    - Oily component may be combusted or ozonized.
- Landfarming is also used.
    - Oily waste is spread out on soil and microbes are allowed to degrade it.
    - Persistent organic compounds accumulate.
    - Volatile organics evaporate.
    - Environmental impact and land costs are issues.
- Treatment with activated charcoal may be considered.

Persistent Organic Pollutants

- Many are toxic.
- Can originate in pesticide manufacture.
- Classified as persistent because they are resistant to oxidation.
    - Do not undergo biological degradation
    - Survive treatment with most chemical oxidants.
    - Can bioaccumulate.
- Therefore waste management strategies are focussed on concentrating these.
    - Activated charcoal is used.
    - Waste stream passes over granulated activated carbon bed.
    - Output of the bed is monitored to determine when breakthrough occurs and bed needs to be replaced.
    - A second bed of activated charcoal is usually in series with monitor of the first bed to ensure that the organic does not get into the environment.
- This treatment merely concentrates the organic, but does not destroy it.
- When breakthrough occurs, the saturated bed is now hazardous solid waste which must be disposed of.
    - Landfilling may not be allowed.
    - Activated charcoal may be incinerated at high temperature to destroy the persistent organic compound.
    - Under properly controlled conditions, the charcoal may be partially burned, which volatilizes the organics which are then subjected to hight temperature combustions. This allows partial recovery of the charcoal for reuse.
- Another approach is chemical treatment of the organics with the intent to degrade them.
    - These methods must be nonselective and work on the entire spectrum of compounds.
- Among the methods considered are:
    - Oxidation with UV and hydrogen peroxide or ozone.
    - Oxidation catalyzed by a semiconductor.
    - Electrochemical oxidation.
    - All of these methods are expensive.

UV assisted oxidation

- Waste stream is aerated and the oxidizing agent (hydrogen peroxide or ozone) is introduced.
- Waste stream is then passed through a quartz tube illuminated by high pressure mercury lamps which are the source of the UV radiation.
- The UV photon promote the formation of OH radicals.
  $$\mathrm{H_2O_2(aq) + h\nu \rightarrow 2\ OH(aq)}$$
- These aqueous phase OH radicals initiate degradation of the organic by abstracting H atoms.
- Since the solution is aerated, the adduct with oxygen is readily formed.
  $$\mathrm{OH(aq) + RH(aq) \rightarrow H_2O + R\cdot}$$

$$R\cdot + O_2 \rightarrow ROO\cdot \rightarrow \text{further oxidation}$$

- This method can be used to destroy aromatic N compounds.
- Costs include mercury lamps, the oxidizing agent, and the electrical energy to run the lamps.

Catalytic Oxidation with TiO_2

- OH is produced by irradiation of water containing a suspension of TiO_2 with light of wavelength near 400 nm (i.e. visible).
  - This radiation promotes an electron to the valence band, leaving behind an electron hole at the site of absorption and a free electron.
  - This hole is filled with an electron from a hydroxide ion, producing an OH radical.
  - The free electron is taken up by an electron acceptor (EA) species such as O_2.
  - Competing with these is the recombination of electrons and holes.
  - The reactions of the interest are:

$$h^+ + OH^-(aq) \rightarrow OH\cdot(aq)$$
$$e^- + EA \rightarrow EA^-$$

  - OH initiate H abstraction while O_2^- furthers the oxidation.

Electrochemical Oxidation

- Ag(II) is a powerful oxidizing agent.
  - Produces OH.
- The reaction sequences are:

$$Ag^{2+} + NO_3^- \rightarrow Ag^+ + NO_3$$
$$NO_3^- + H_2O \rightarrow NO_3 + H^+ + OH$$
$$Ag^{2+} + H_2O \rightarrow Ag^+ + H^+ + OH$$

- Energy is input to convert Ag^+ to Ag^{2+}.

Air Stripping

- Has the effect of changing water pollution to air pollution.
  - Acceptable for compounds that are naturally oxidized in air.
  - Unacceptable and controversial for compounds that do not break down readily in air.
- Feasible for compounds where equilibrium favours the gas phase.

$$X(aq) \rightleftharpoons X(g)$$

$$K'_H = \frac{1}{K_H} = \frac{X(g)}{X(aq)}$$

  - The larger K'_H is, the more effective air stripping can be.
  - Increasing the temperature increases K'_H (i.e. steam stripping).
  - Steam stripping is convenient to apply to process streams that are already warm.
- Air requires further treatment before being exhausted.

  - Catalytic oxidation
  - Wet air oxidation by heating to temperatures at which complete oxidation can occur.
  - Biofilm treatment.

Inorganic Aqueous Wastes

- Three major classes:
  - Ammonia
  - Cyanide
  - Heavy Metals

Ammonia

- Three methods of addressing NH_3 in aqueous waste.
  - Air stripping
  - Nitrification
  - Breakpoint Chlorination
- Nitrification involves microbial oxidation of ammonia to nitrate.
  - This differs from natural nitrification in soil which gives NO and N_2.
- Breakpoint chlorination involves the oxidation of ammonia by HOCl:
$$2\ NH_3(aq) + 2\ HOCl(aq) \rightarrow N_2(g) + 3\ HCl(aq) + 3\ H_2O(l)$$
  - The oxidation occurs stepwise with intermediate formation of NH_2Cl and $NHCl_2$, which in turn react with each other to form N_2,
$$NH_3(aq) + HOCl(aq) \rightarrow NH_2Cl(aq) + H_2O(l)$$
$$NH_2Cl(aq) + HOCl(aq) \rightarrow NHCl_2(aq) + H_2O(l)$$
$$NH_2Cl(aq) + NHCl_2(aq) \rightarrow N_2(g) + 3\ HCl(aq)$$
- The term “breakpoint” refers to the behaviour of the chlorine residual in the solution as a function of the chlorine dose.
  - Initially the chlorine is taken up as NH_2Cl which is an active form of chlorine.
  - As $NHCl_2$ is formed, it reacts with NH_2Cl to form N_2.
  - Thus the amount of active chlorine drops as NH_2Cl is used up.
  - The point where active chlorine drops to zero is the breakpoint and all NH_3 is converted to N_2.

Cyanide

- Used in a number of industries:
  - mining
  - electroplating
  - metal finishing
- Usually gives rise to aqueous waste contaminated by both cyanide and heavy metal.
- Cyanide is removed by oxidation:
$$CN^-(aq) + HOCl(aq) \rightarrow OCN^-(aq) + HCl(aq)$$

$$CN^-(aq) + Cl_2(aq) + H_2O(aq) \rightarrow OCN^-(aq) + 2\ HCl(aq)$$

- Cyanate (OCN^-) itself hydrolyzes quite easily.
$$CN^-(aq) + H^+(aq) + H_2O(l) \rightarrow NH_3(aq) + CO_2(aq)$$

Heavy Metals

- Generally refers to metal with atomic numbers greater than 26 (Iron).
  - Common usage usually includes vanadium and chromium.
- Many metals with industrial use have been discharged into the environment throughout history.
  - Electroplating can involve copper, chromium, silver, nickel, cadmium.
  - Catalysts include copper, gold, silver, platinum, vanadium, mercury, and nickel.
  - Lead is used in batteries and was formerly used as a gasoline additive.
  - Mercury is used in batteries, switches, and the manufacture of chlorine and sodium hydroxide.
- Metal ions can be precipitated with appropriate anions.
  - Metal sulphides are very insoluble and may be formed by bubbling H_2S through the solution.
$$H_2S(g) + M^{2+}(aq) \rightarrow MS(s) + 2\ H^+$$
  - Precipitation is more efficient at high pH, so lime is used prior to treatment with H_2S.
  - The resulting sludge must be disposed of.

Landfills

- Landfilling refers to dumping on the ground.
- May be secured or unsecured
- May have been regulated or unregulated
- May be done properly or improperly

  - Love Canal (improper landfilling of industrial waste)
  - Times Beach (improper disposal of waste oil)
  - Valley of the Drums (improper disposal of chemicals in unprotected steel drums).
- There is legacy of sites that are unsecured and unengineered.
  - No record of what may have been dumped
  - No means of managing leachate.
- Many sites in North America are "sanitary landfill sites"
  - The focus in on the prevention of disease.
  - Waste is periodically covered with soil to prevent access by rodents.
  - When a site is full, it is covered and planted with vegetation.
  - Meanwhile anaerobic decomposition continues with concomitant settling of the ground and release of gases such as methane which can pose an explosion hazard.

  - These hazards limit subsequent use of the land.

- Per capita waste generation in North America is 1.8 kg per day.
- Historically site selection for landfills and hazardous waste sites has been based on convenience and lack of value of the land for other purposes.
  - This led to wetlands and swamps being used for landfills.
  - In the case of dumping of drums of chemicals, this led to contamination of ground water when the drums corroded.
- Different soils have different properties:
  - Clays are relatively impervious.
  - Sand and gravel are porous.
- Rain and snow seep into landfills and leach soluble material.
  - Depending on the overlying soil structure, the leachate may contaminate ground water and lead to long distance transport of toxins.
- Historically landfills have accepted industrial waste with few (if any) restrictions.
  - Currently landfills are regarded as the least desirable way of dealing with industrial waste.

Secure Landfills

- Carefully planned and operated.
- Sites are selected with a view of protecting aquifers.
  - Bottom liner of impervious clay.
  - Leachate is collected and treated.
  - Surrounding aquifer is monitored.
- Secure operation controls what is dumped at the landfill.
  - Hazardous waste “knowingly” accepted.
  - Fees associated with dumping cover monitoring costs and leachate treatment.
- When landfill is full, it is capped with impervious clay.
  - Minimizes leachate by preventing infiltration by snow and rain.
  - Gaseous anaerobic decay products are collected and vented to prevent cracking of the cap.
  - Methane can be used for cogeneration.
  - Volatilized organics can contribute to air pollution.
- Hazardous waste dumps are further engineered for particular waste.
  - Clay base assessed for transport properties of the specific substances.
  - Monitoring
  - Leachate treatment and collection.
- Historically hazardous waste disposal has been poorly managed or mismanaged.

Love Canal

- Near Niagara Falls, New York.

- Love Canal was initiated in the late 1800's by William Love to bypass Niagara Falls and generate hydroelectric power.
  - Project went bankrupt leaving a 1.6 km long 15 m wide ditch varying in depth from 3 to 13 m.
- When hydroelectric power did come to the area, industry followed.
  - Hooker Chemical manufactured chlorine and organochlorine compounds.
  - Chlorine is manufactured from NaCl by electrolysis using a flowing mercury cell.
- During World War II, Love Canal began to be used as a chemical dump.
  - 20,000 tonnes of waste accumulated.
  - Love Canal capped with clay.
- Love Canal later developed.
  - Road construction disrupted clay cap.
  - Homes constructed
  - School built on top of canal.
- By the 1970's problems were evident.
  - Toxic chemicals were found in the schoolyard and in the basements of homes.
  - Residents were evacuated and relocated, and the school closed.
  - Eventually homes were expropriated and site sealed off.
- Lawsuits continue.
- Similar scenarios are being played out across Canada and around the world.
- In Canada, some sites of concern are:
  - Former dump sites developed as residential areas.
  - Sydney Tar Ponds
  - "Valleys of Drums" associated with World War II military installations throughout the north.
  - Former gas station sites.