

Lecture 13. Hydrological cycle. Basic aqueous chemistry.

Objectives:

1. The hydrological cycle.
2. Clouds.
3. Basic aqueous chemistry:
Acids and bases. Acidity and pH.
The solubility of gases.

Readings: Turco: p. 317, 80-81, 261-267; Brimblecombe: p. 82-100

1. The hydrological (or water) cycle plays a fundamental role in the geochemical cycling of elements.

Water on the Earth:

oceans	97%
polar ice caps	2.1%
atmosphere	0.001%
others	0.6%

- Despite the small amount of water in the atmosphere, the transport and phase distribution of water are some of the most important features of Earth's climate.

Water exists in three different physical states (phases) :

gaseous (water vapor);

liquid (water drops, clouds, fogs, rain, aerosols);

solid (ice, snow)

Phase (state) changes of water:

vapor -> liquid (**condensation**, exothermic process)

liquid -> vapor (**evaporation or vaporization**, endothermic process)

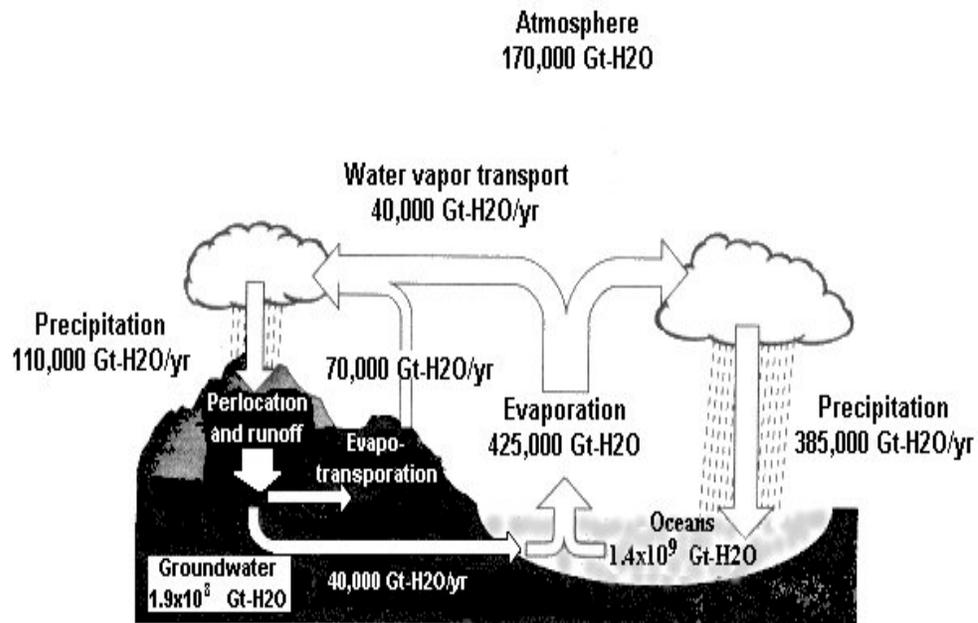
liquid -> solid (**freezing or crystallization**, exothermic process)

solid -> liquid (**melting or fusion**, endothermic process)

vapor -> solid (**deposition**)

solid -> vapor (**sublimation**)

Figure 13.1 The hydrological cycle on the Earth (Turco 1997).



2. Clouds.

Clouds are one of the most significant elements of the atmosphere system, playing several key roles:

- Clouds are a major factor in the Earth's radiation budget, reflecting sunlight back to space or blanketing the lower atmosphere and trapping infrared radiation emitted by the Earth's surface (discussed in Lecture 31-32).
- Clouds deliver water from the atmosphere to the Earth's surface as rain or snow and thus a key step in the hydrologic cycle.
- Clouds scavenge gaseous and particulate materials (aerosols) and return them to the surface (wet deposition).
- Clouds provide a medium for aqueous-phase chemical reactions and production of secondary species.
- Clouds affect significantly vertical transport in the atmosphere. Updrafts and downdrafts associated with clouds determine in a major way the vertical redistribution of trace species in the atmosphere.

Major cloud characteristics are *cloud type; cloud coverage; liquid water content of cloud; cloud droplet concentration; cloud droplet size.*

NOTE: Liquid water content of cloud; cloud droplet concentration; cloud droplet size are called **cloud microphysical characteristics**.

- Cloud droplet sizes vary from a few micrometers to 100 micrometers with average diameter in 10 to 20 μm range.
- Cloud droplet concentration varies from about 10 cm^{-3} to 1000 cm^{-3} with average droplet concentration of a few hundred cm^{-3} .

NOTE: Marine clouds are characterized by relatively smaller droplet concentration and larger diameters, where continental clouds tend to have smaller droplets.

Table. Types and properties of cloud.

Type	Height of base (km)	Freq. over oceans (%)	Coverage over oceans (%)	Freq. over land (%)	Coverage over land (%)
low level:					
Stratocumulus (Sc)	0-2	45	34	27	18
Stratus (St)	0-2	(Sc+St)	(Sc+St)	(Sc+St)	(Sc+St)
Nimbostratus (Ns)	0-4	6	6	6	5
mid level:					
Altostratus (As)	2-7	46	22	35	21
Altostratus (As)	2-7	(Ac+As)	(Ac+As)	(Ac+As)	(Ac+As)
high level:					
Cirrus (Ci)	7-18	37	13	47	23
Cirrostratus (Cs)	7-18	Ci+Cs+Cc	Ci+Cs+Cc	Ci+Cs+Cc	Ci+Cs+Cc
Cirrocumulus (Cc)	7-18				
clouds with vertical development					
Cumulus (Cu)	0-3	33	12	14	5
Cumulonimbus (Cb)	0-3	10	6	7	4

NOTE: Clouds cover approximately 60% of the Earth's surface. Average global coverage over the oceans is about 65% and over the land is about 52%.

The occurrence of clouds shows dramatic geographical variation. Clouds form and evaporate repeatedly. Only a small fraction (around 10%) of the clouds actually generate precipitation.

Liquid water is one of the most important cloud characteristics for atmospheric chemistry.

- ◆ The liquid water content of typical clouds, given by the symbol L and often abbreviated LWC, varies from approximately 0.05 to 3 g(water) m⁻³, with most of the observed values in the 0.1 to 0.3 g(water) m⁻³ region.
- ◆ The liquid water content is often expressed as liquid water mixing ratio w_1 in (volume water/volume air) and it is related to L by

$$w_1 \text{ (vol water/vol air)} = 10^{-6} L \text{ (g m}^{-3}\text{)}$$

The cloudwater mixing ratio w_1 varies from 5×10^{-8} to 3×10^{-6} .

2. Basic aqueous chemistry.

Solution is a mixture of atoms, ions, or molecules of two or more substances.

Ions are electrically charged atom or group of atoms.

Anion is a negatively charged ion. Cation is a positively charged ion.

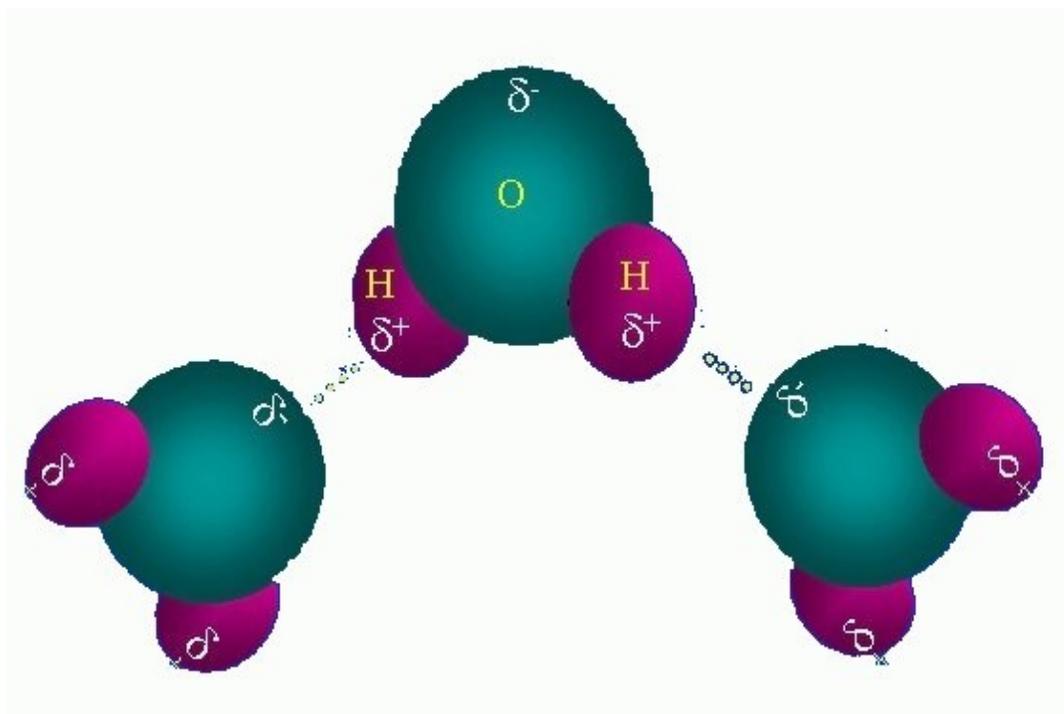
NOTE: ions and ionic compounds were discussed in Lecture 6.

Aqueous solution refers to the dissolution of a particular substance, the **solute**, in water, the **solvent**.

Aqueous chemistry is the chemistry of reactions which take place in aqueous solution.

- ◆ Special properties of water: the ability of water molecules to stick together through **hydrogen bond**. Hydrogen bond forms between water molecules because of their strong polarization.

Figure 13.2 Hydrogen bonding between water molecules. The hydrogen atom of one water molecule is weakly attracted by the oxygen atom of another water molecule.



Upon dissolution in water a number of species **dissociate** into ions.

Water itself dissociate on hydrogen ion, H^+ , and a hydroxide ion, OH^- :

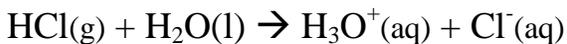


- Water is an **amphoteric** substance: can behave either as and acid or as a base.

Acids are the proton (H^+) donors, and bases (alkalis) are the proton acceptors.

Water as a base:

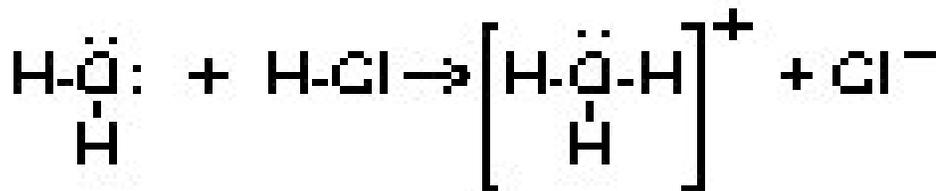
For instance, gaseous HCl dissolves in water:



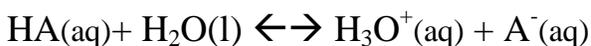
In this reaction, each HCl molecule donates a proton to a water molecule, so HCl qualifies as an acid. Molecule of water accepts proton, so in this case it is a base.

H_3O^+ is called the **hydronium ion**.

How it works (shown by Lewis structure):



The general reaction that occurs when an acid is dissolved in water :



Acid	Base	Conjugate	Conjugate
		acid	base

NOTE:

1. The conjugate base is everything that remains of the acid molecule after a proton is lost;
2. The conjugate acid is form when the proton is transferred to the base;
3. The conjugate acid-base pair consists of two substances related to each other by donating and accepting of a single proton;
4. Often H_2O is omitted in the reaction equations, and $\text{H}^+(\text{aq})$ is used instead H_3O^+ , so the reaction above will look as : $\text{HA(aq)} \rightleftharpoons \text{H}^+(\text{aq}) + \text{A}^-(\text{aq})$

Water as an acid:

For instance, gaseous NH_3 dissolves in water:



In this reaction, each water molecule donates a proton to NH_3 molecule, so H_2O molecule qualifies as an acid. Molecule of NH_3 accepts proton, so in this case it is a base.

Arrhenius definitions for acids and bases (less general, but more straight forward):

when dissolved in water, acids produce positively charged hydrogen ion (H^+), and bases produce negatively charged hydroxide (OH^-)

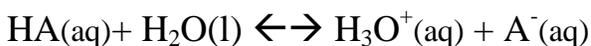
Examples:

bases: potassium hydroxide (KOH); sodium hydroxide (NaOH);

acids: sulfuric acid (H_2SO_4); formic acid (HCOOH), hydrobromic acid (HBr)

Acid strength:

is defined by the equilibrium position of its dissociation reaction:



the equilibrium expression is

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

Strong acid is one for which this equilibrium lays far to the right: means that almost all of the original HA is dissociated at equilibrium. Conversely, a **weak acid** is one for which equilibrium lies far for the left.

◆ Important strong acids in the atmosphere:

sulfuric acid (H_2SO_4); nitric acid (HNO_3), and hydrochloric acid (HCl).

◆ Important weak acids in the atmosphere:

carbonic acid (H_2CO_3); sulfurous acid (H_2SO_3).

NOTE: a strong acid yields a weak conjugate base (whose conjugate base is a much weaker base than water), and a weak acid yields a relatively strong base which is much stronger than water)

Acidity and pH

For pure water:



at equilibrium

$K_w = [\text{H}^+] [\text{OH}^-] / [\text{H}_2\text{O}]$, where $K_w = 1.82 \times 10^{-16}$ M at 298 K.

NOTE: the customary unit of the concentration in aqueous solution is moles per liter of water, called the **molar unit** and abbreviated as M.

However, in the reaction above the concentration of H_2O molecules is so large (around 55.5 M), and so few ions are formed, that $[\text{H}_2\text{O}]$ is virtually constant. Therefore, the molar concentration of pure water is incorporated into the equilibrium constant to give

$K_w^* = [\text{H}^+] [\text{OH}^-]$, where $K_w^* = K_w [\text{H}_2\text{O}] = 1.0 \times 10^{-14} \text{ M}^2$ at 298 K.

Each molecule of water produces H^+ and OH^- , therefore

$[\text{H}^+] = [\text{OH}^-]$,

thus at 298 K , $[H^+] = [OH^-] = 1.0 \times 10^{-7} \text{ M}$

Defining the pH of water as

$$\text{pH} = -\log[H^+]$$

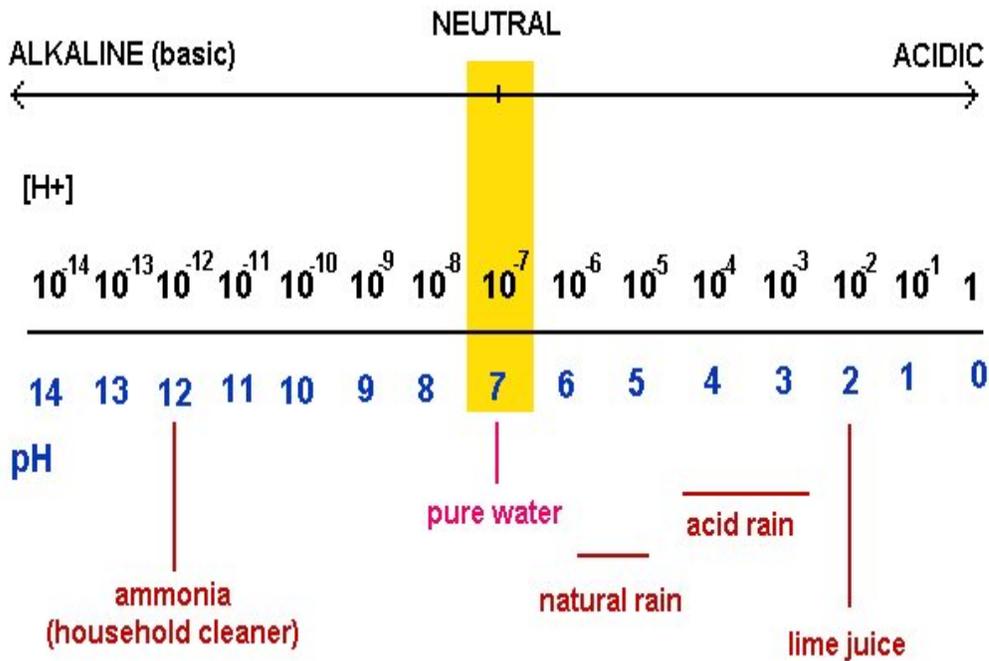
we see that **pH=7** for pure water at 298 K.

This fundamental relationship between $[H^+]$ and $[OH^-]$ allows to establish a universal scale of pH.

The pH scale is a compact way to represent solution acidity or alkalinity.

- Since pH is a log scale based on 10, the pH changes by 1 for every power of -10 change in $[H^+]$. For instance, a solution of pH 3 has an H^+ concentration 10 times that of solution of pH 4 and 100 times that a solution of pH 5.
- Since pH is defined as $-\log[H^+]$, the pH decreases as $[H^+]$ increases.
- Each unit of increase on the pH scale implies a factor of ten decreases in acidity, or hydrogen ion concentration, and increase in alkalinity, or hydroxide ion concentration.

Figure 13.3 The pH scale and pH values of some common substances.



- Some acid vapors can be produced photochemically in the air and later dissolve in cloud droplets. Acids may also be formed directly in droplets from their gaseous precursors. The latter process depends on *gas solubility* which is described by a relationship known as *Henry's law*.

The equilibrium of a species A between the gas and aqueous phase can be represented by



Henry law states that, at equilibrium, the partial pressure of the gas above a solution of it is proportional to the concentration of the gas in the solution:

$$[A(aq)] = H_A p_A$$

where p_A is the partial pressure of A in the gas phase (atm), and $[A(aq)]$ is the aqueous-phase concentration of A (mol L^{-1}) in equilibrium with p_A .

H_A is the Henry's law coefficient in ($\text{mol L}^{-1} \text{atm}^{-1}$) or (M atm^{-1}).

NOTE: by definition above, soluble gases have large Henry's law coefficients.

Table. Henry's law coefficients of some atmospheric gases.

Species	H (M atm^{-1}) at 298K
O ₂	1.3×10^{-3}
NO	1.9×10^{-3}
NO ₂	1.0×10^{-2}
O ₃	1.13×10^{-2}
SO ₂	1.23
OH	25.0
NH ₃	62.0
HCl	727.0
H ₂ O ₂	7.45×10^4
HNO ₃	2.1×10^5
NO ₃	2.1×10^5

NOTE:

1. Henry's law coefficient depends on temperature. In general, H_A increases as temperature decreases, reflecting a greater solubility of a gas at lower temperature.
2. Henry's law coefficients in the Table above do not account for dissociation or other aqueous-phase transformation (i.e., regardless the subsequent fate of A once dissolved).

Solubility benchmark for atmospheric applications:

the distribution of a species between gas and aqueous phase in a typical cloud.

Species that reside mainly in the gas phase are considered **insoluble**, and species that are almost exclusively in the aqueous phase are considered **very soluble**. Intermediate species, with significant fractions in both phases, are considered **moderately soluble**.

For atmospheric applications:

Insoluble species have $H_A < 1000 \text{ M atm}^{-1}$

Moderately soluble have $1000 \text{ M atm}^{-1} < H_A < 10,000 \text{ M atm}^{-1}$

Very soluble have $H_A > 10,000 \text{ M atm}^{-1}$

NOTE: it does not apply that only very soluble gases are important in atmospheric aqueous-phase chemistry.

- If gases dissociate or react in aqueous solution then their solubility can be much enhanced (see example below for $\text{CO}_2/\text{H}_2\text{O}$ equilibrium)

Typical steps of atmospheric aqueous-chemistry :

1. Dissolution of gas A to form hydrated molecules ($\text{A} \cdot \text{H}_2\text{O}$)
2. Dissociation of dissolved gas $\text{A} \cdot \text{H}_2\text{O}$ to form ions
3. Oxidation-reduction reactions of formed ions

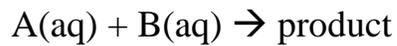
NOTE: $\text{A}(\text{aq})$ and $\text{A} \cdot \text{H}_2\text{O}$ are the alternative notations for the same chemical species

Rates of a reaction of aqueous-phase are expressed in

moles per liter (M) of solution per second

but it is often converted to the units of gas-phase reactions when comparing gas-phase and aqueous phase reaction rates.

For instance, gas A dissolves in water and then reacts with B(aq)



$$\text{rate} = k [A(aq)] [B(aq)],$$

here rate is in $M s^{-1}$, the aqueous-phase concentrations $[A(aq)]$ and $[B(aq)]$ are in M,

and the reaction rate constant k is in $M^{-1} s^{-1}$.

The equivalent gas-oxidation rate at total pressure of 1 atm is

$$\text{rate}^* = 3.6 \times 10^6 L R T \text{ rate},$$

where rate^* is in ppb h^{-1} , L is the liquid water content in g m^{-3} ,

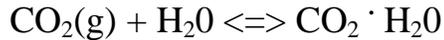
R = 0.082 Liter $K^{-1} \text{mole}^{-1}$, and T is in K.

Aqueous-phase chemical equilibrium

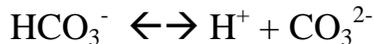
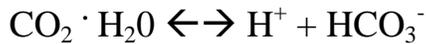
For instance,

“Pure” rainwater: carbon dioxide/water equilibrium.

Dissolution of CO₂:



Dissociation of CO₂ · H₂O:



NOTE: that CO₂ · H₂O dissociates twice to form the carbonate and bicarbonate ions.

The equilibrium constant for the above reactions are:

$$K_{\text{hc}} = H_{\text{CO}_2} = [\text{CO}_2 \cdot \text{H}_2\text{O}] / p_{\text{CO}_2}$$

$$K_{\text{c1}} = [\text{H}^+] [\text{HCO}_3^-] / [\text{CO}_2 \cdot \text{H}_2\text{O}]$$

$$K_{\text{c2}} = [\text{H}^+] [\text{CO}_3^{2-}] / [\text{HCO}_3^-]$$

where K_{hc} is the equilibrium constant for the hydrolysis of CO₂ with incorporated liquid water concentration (note that K_{hc} is identical here to the Henry's law coefficient for carbon dioxide, H_{CO_2}), K_{c1} and K_{c2} denote the first and second dissociation equilibrium constants for dissolved CO₂.

The concentrations of species in solution are given by

$$[\text{CO}_2 \cdot \text{H}_2\text{O}] = H_{\text{CO}_2} p_{\text{CO}_2}$$

$$[\text{HCO}_3^-] = K_{\text{c1}} [\text{CO}_2 \cdot \text{H}_2\text{O}] / [\text{H}^+] = K_{\text{c1}} H_{\text{CO}_2} p_{\text{CO}_2} / [\text{H}^+]$$

$$[\text{CO}_3^{2-}] = K_{\text{c2}} [\text{HCO}_3^-] / [\text{H}^+] = K_{\text{c1}} K_{\text{c2}} H_{\text{CO}_2} p_{\text{CO}_2} / [\text{H}^+]^2$$

The total dissolved carbon dioxide [CO₂^T] is then

$$\begin{aligned} [\text{CO}_2^{\text{T}}] &= [\text{CO}_2 \cdot \text{H}_2\text{O}] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] = \\ &= H_{\text{CO}_2} p_{\text{CO}_2} (1 + K_{\text{c1}} / [\text{H}^+] + K_{\text{c2}} / [\text{H}^+]^2) \end{aligned}$$

Let's define the **effective Henry's law constant** for CO₂, $H_{\text{CO}_2}^*$, as

$$H_{\text{CO}_2}^* = H_{\text{CO}_2} (1 + K_{\text{c1}} / [\text{H}^+] + K_{\text{c2}} / [\text{H}^+]^2)$$

then the total dissolved carbon dioxide is given by

$$[\text{CO}_2^T] = H_{\text{CO}_2}^* p_{\text{CO}_2}$$

$H_{\text{CO}_2}^*$ is always exceeds the Henry's law constant

$$H_{\text{CO}_2}^* > H_{\text{CO}_2}$$

therefore the total amount of CO_2 dissolved always exceed that predicted by Henry's law for CO_2 alone.

NOTE: H_{CO_2} depends only on T, while $H_{\text{CO}_2}^*$ depends on T and the solution pH.

We can calculate pH of solution for representative vapor pressure of CO_2 using the electroneutrality equation for the solution:

$$[\text{H}^+] = [\text{OH}^-] + [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}]$$

For $p_{\text{CO}_2} = 350$ ppm at $T=298$ K : **pH = 5.6 is often called the pH of 'pure' rainwater.**

- Most important chemical transformation in cloud water:



NOTE: aqueous-phase chemistry of sulfur will be discussed in Lectures 22-24 on acid rain.