

## CIVE 3331 Environmental Engineering

CIVE 3331 - ENVIRONMENTAL ENGINEERING  
Spring 2003

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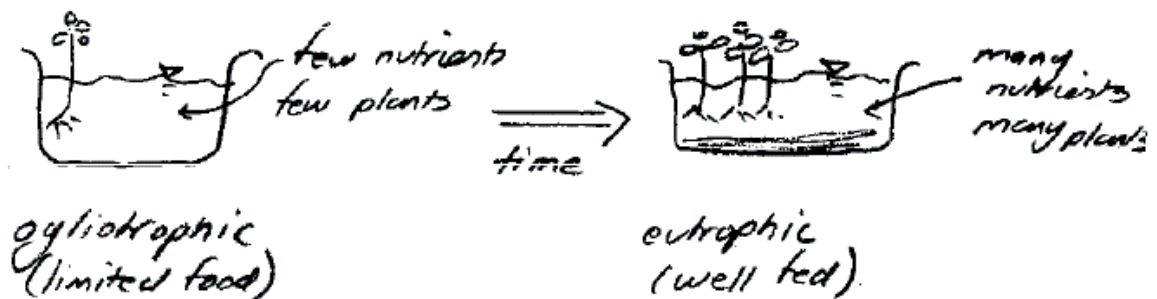
Purpose: Lecture #8 CIVE3331

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**Lakes and Reservoirs**

Lakes and reservoirs experience a natural aging process called eutrophication. Human activity accelerates the process by adding wastes, agricultural runoff, etc. that supplies nutrients at a rate much greater than occurs in nature. The accelerated process is called anthropogenic eutrophication.

Figure 1 is a sketch of the eutrophication process starting from a oligotrophic state to the eutrophic state.



**Figure 1. Eutrophication Process**

Factors that control eutrophication are:

- 1) Light penetration; related to water clarity (turbidity)
- 2) Nutrient supply

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## 3) Depth

Sufficiently deep lakes have two zones, the euphotic zone (photosynthesis produces more O<sub>2</sub> than used during respiration) and the profundal zone (respiration uses more O<sub>2</sub> than produced by photosynthesis). The light penetration affects the location of the zonal interface and the depth of this interface is called the light compensation level.

Figure 2 is a sketch illustrating the relationship of light penetration and depth.

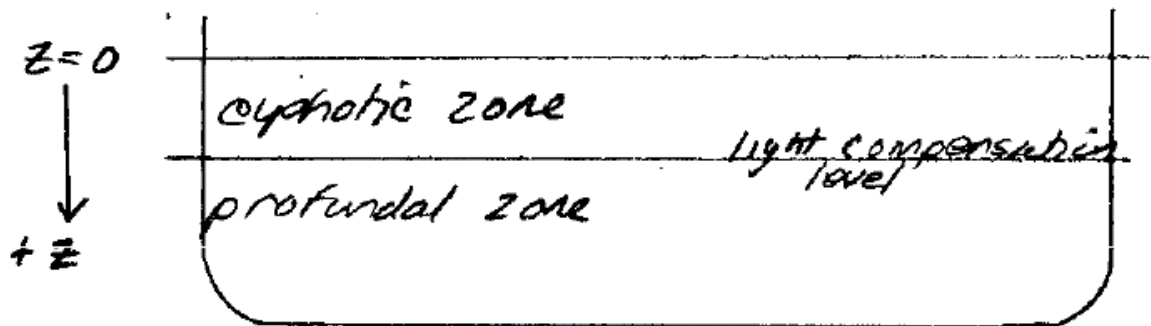


Figure 2. Light Compensation Depth

### Photosynthesis and Limiting Nutrients

The nutrient supply is a principal factor in lake health. Growth is limited by the least available nutrient. Engineering control of the limiting nutrient can control the rate of eutrophication. Control of non-limiting nutrient is only useful if it can be reduced enough to become the limiting nutrient.

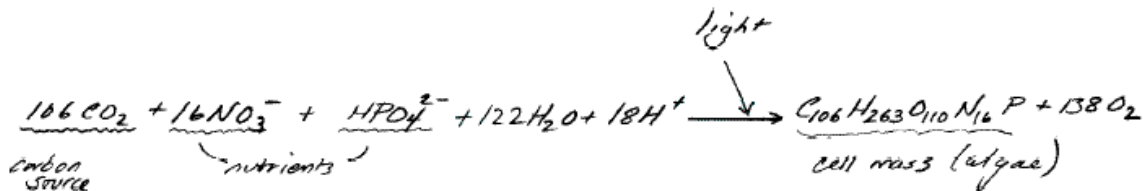


Figure 3. Photosynthesis Model

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If we calculate the mass of N versus P in algae we will discover it takes 7 times more N than P (by mass) to produce algae. Thus control of P can greatly impact algae growth ( a surrogate for eutrophication).

From such calculations the following rules-of-thumb are indicated:

- 1)  $N \sim 10 \times P$ , then P is the limiting nutrient
- 2)  $N < 10 \times P$ , then N is limiting nutrient
- 3) In addition to the relative abundance, if absolute abundance exceeds 0.3 mg/L-N and 0.015 mg/L-P then one expects algal blooms.

### Simple Phosphorous Model

Usually modeling is used to estimate the amount of control to apply to reduce the eutrophication rate.

Generally, if  $P < 0.01$  mg/L then the system is OK, if  $P > 0.02$ mg/L then too much

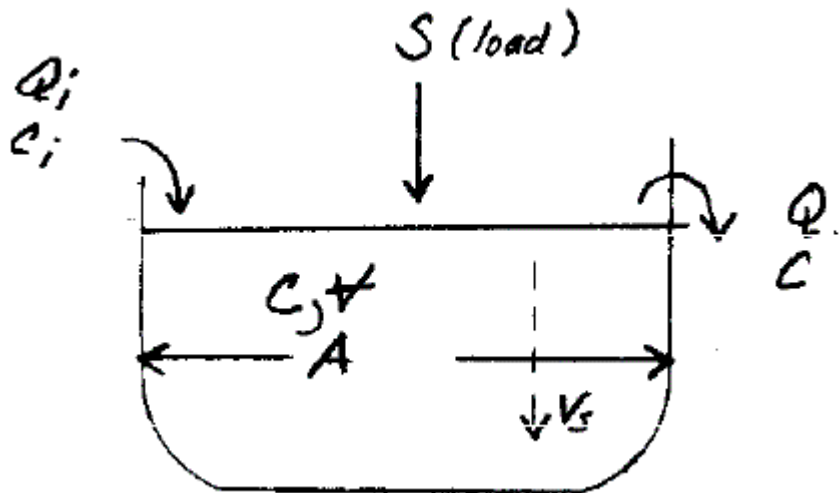


Figure 4. Simple Phosphorous Model

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Figure 4 is a sketch of a lake that is used for elementary phosphorous modeling. If we write a mass balance in the water (note the settling velocity in the sketch) we can calculate the concentration of P in the water.

$$\text{Inflow:} \quad S \quad + \quad Q_i C_i$$

$$\text{Outflow (from water)} \quad QC \quad + \quad v_s AC$$

The second term on the outflow represents the fraction of P that settles out of the water column. P is known to attach to solids in the water and settle out with time. It can be considered as a mass transfer term in the equation. The Mass Rate Balance is then :

$$\frac{dVC}{dt} = S + Q_i C_i - QC - v_s AC$$

At equilibrium the time derivative vanishes and we can solve for the equilibrium concentration as

$$C = \frac{S + Q_i C_i}{Q + v_s A}$$

Example

Lake with  $A = 80 \cdot 10^6 \text{ m}^2$ ,  $15 \text{ m}^3/\text{s}$  inflow;  $C = 0.01 \text{ mg/L}$ . Load of  $1 \text{ g/s}$ , settling rate is  $10 \text{ cm/yr}$ . Find P at equilibrium; % removal at load to keep lake at  $0.01 \text{ mg/L}$ .

①  $C = \frac{S + Q_i C_i}{Q + v_s A} = \frac{1000 \text{ mg/s} + 0.01 \text{ mg} \cdot \frac{1000 \text{ L}}{\text{m}^3} \cdot \frac{15 \text{ m}^3}{\text{s}}}{\frac{15 \text{ m}^3}{\text{s}} + \frac{10 \text{ cm}}{\text{yr}} \cdot \frac{1 \text{ d}}{365 \text{ d}} \cdot \frac{80 \cdot 10^6 \text{ m}^2}{86400 \text{ sec}}} = \frac{28.48 \text{ mg/s}}{40.367 \text{ m}^3/\text{s}} = 0.0284 \text{ mg/L}$

②  $\frac{x \text{ mg/s} + 150 \text{ mg/s}}{40.367 \text{ m}^3/\text{s}} = 10.00 \text{ mg/m}^3$  Solve for  $x$

$x = 253.6 \text{ mg/s}$   $\therefore$  % removal =  $\frac{1000 - 253.6 \text{ mg/s}}{1000 \text{ mg/s}} \times 100 = 74.6\%$

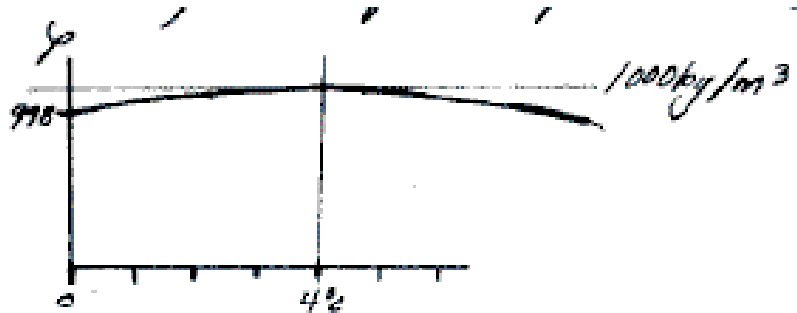
**Figure 5. Example Simple P Model**

This model neglects stratification, seasonal fluctuation in inputs, and mixing. Such features are beyond the scope of this lecture, but one should be aware of the existence of such processes.

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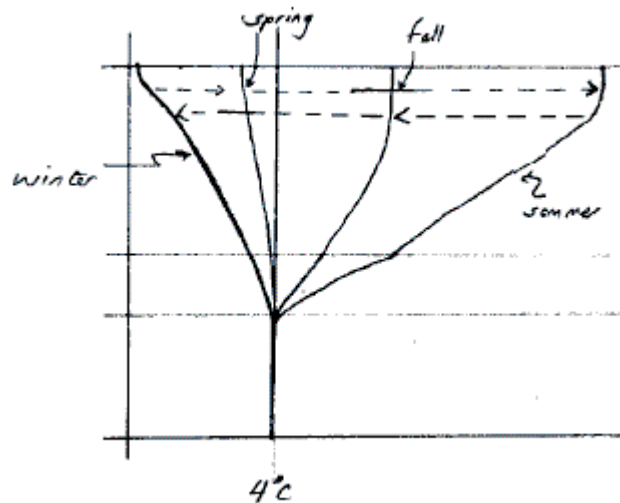
**Thermal Stratification**

Water density-temperature dependence is not monotonic – it has a peak value at 4°C. At this temperature water “sinks” relative to cooler or warmer water and creates a distinct temperature layering in lakes that inhibits vertical mixing.



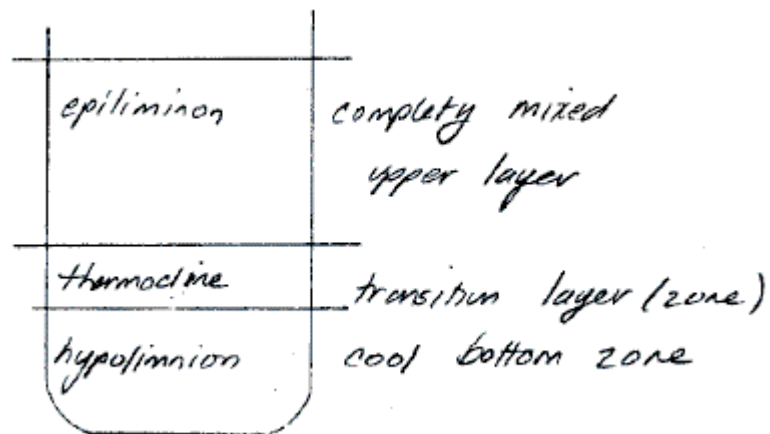
**Figure 6. Density-temperature for water**

Between spring and summer and summer and fall the vertical profile makes mixing (called overturn) possible. During the turnover materials in the sediment and lower layers are resuspended and mixed throughout the water column.



**Figure 7. Temperature-depth profile(s) in a lake**

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**Figure 8. Layer names in stratified lake**

If turnover is rare then  $H_2S$ ,  $CH_4$  and  $CO_2$  can build up in the hypolimnion region. The lake can “burp” and release large volumes of these gasses with catastrophic results.

### **Buffered Systems**

Natural rainfall in equilibrium with atmospheric  $CO_2$  has a pH  $\sim 5.6$ . In recent years rainfall pH has declined, in some cases pH  $< 4.0$ . The reduced pH is caused by  $SO_4$  and  $NO_x$  in the atmosphere changing the chemistry of the rainfall.

If a lake is poorly buffered, it too will experience a decline in pH as the acidic rainfall enters the lake system. Carbonate is one of many natural buffers.

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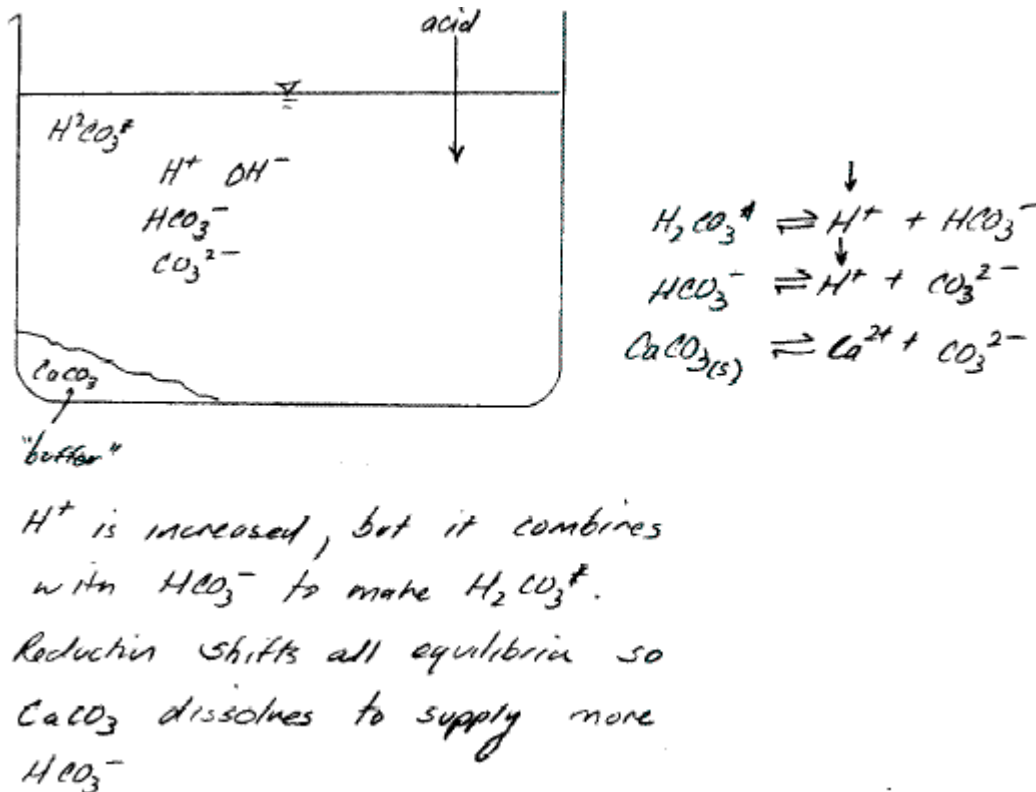
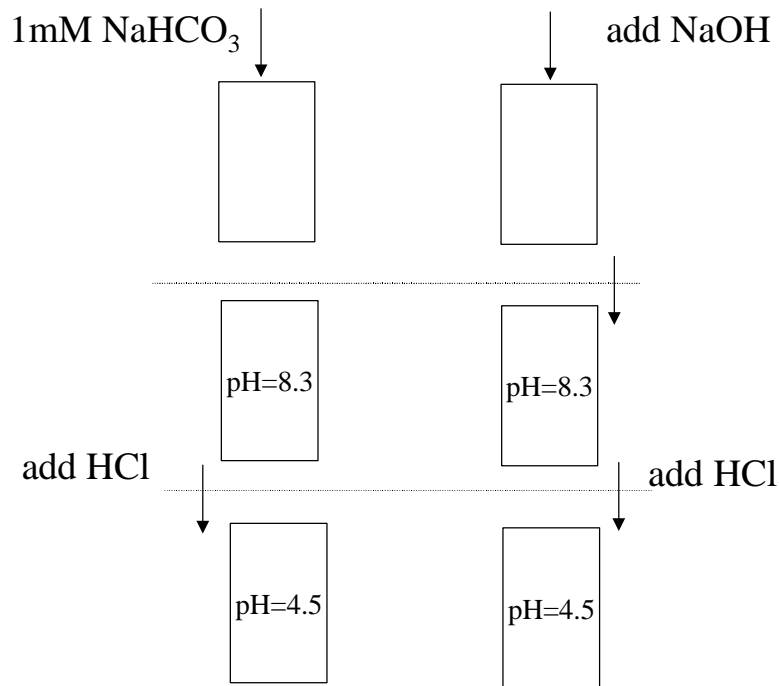


Figure 9. Carbonate Buffering

## Buffering Illustration

Consider two 1L samples. To one we add baking soda and compute its pH. Then we add NaOH to the other sample until it has the same pH. Now we add HCl to both and compute how much HCl is added to each sample. A system that takes a lot of acid (HCl) to cause a change in pH is the "buffered" system. If you read ahead about alkalinity in the water treatment chapter the parallels should be obvious.

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How much HCL in each case?

**Figure 10. Buffering Example**

Analysis for Sample A after addition of baking soda, before addition of acid.

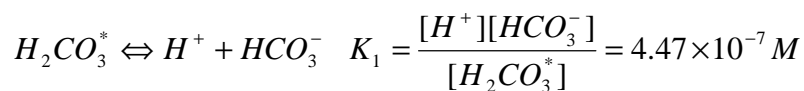
Baking soda has a very high solubility product, so it dissociates completely, therefore the concentrations of [Na] is equal to the moles of soda added.

$$[Na^+] = 10^{-3} M$$

The only source of carbon is assumed to be the soda (ignore atmospheric C, the dissolution process is slow relative to the other equilibrium), so the total carbon balance is

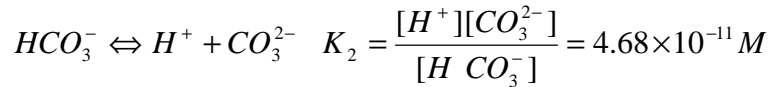
$$[H_2CO_3^*] + [CO_3^{2-}] + [HCO_3^-] = 10^{-3} M$$

Now the usual carbonate species

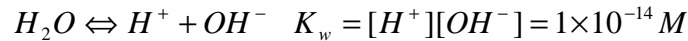




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Water dissociation



Finally the charge balance

$$[H^+] + [Na^+] = [OH^-] + 2[CO_3^{2-}] + [HCO_3^-]$$

Now solve for pH.

The trick is to use the carbon balance and the first equilibrium to express bicarbonate in terms of pH, then by successive guessing at pH solve the charge balance and remaining equilibria. The algebra is

$$[H_2CO_3^*] + [CO_3^{2-}] + [HCO_3^-] = 10^{-3} M \quad \text{Start with carbon balance}$$

$$\frac{[H^+][HCO_3^-]}{4.47 \times 10^{-7}} + \frac{[HCO_3^-]4.68 \times 10^{-11}}{[H^+]} + [HCO_3^-] = 10^{-3} M \quad \text{Incorporate the two acid disassociation}$$

equilibria.

$$[HCO_3^-] = \frac{10^{-3}}{1 + \frac{[H^+]}{4.47 \times 10^{-7}} + \frac{4.68 \times 10^{-11}}{[H^+]}} \quad \text{solve for bicarbonate}$$

Now if we guess a value for pH, we can calculate the  $HCO_3^-$  from the above equation, we can compute the  $CO_3^{2-}$  from its dissociation equation,  $OH^-$  from the water disassociation equation. With the known Na value and these just computed values, compute the value of the left hand side of the charge balance and the right hand side of the charge balance – at the correct pH these two value should be identical.

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	A	B	C	D	E	F	G	H	I	J	K
1	Closed Carbonate System - 1mM NaHCO3 - Find pH										
2			[Na]	1.00E-03							
3	pH	[H <sup>+</sup> ]	[OH <sup>-</sup> ]	[Na]	[HCO <sub>3</sub> <sup>-</sup> ]	[HCO <sub>3</sub> ]	[CO <sub>3</sub> ]	[HCO <sub>3</sub> <sup>+</sup> ]+[HCO <sub>3</sub> ]+[CO <sub>3</sub> ]	[Na]+[H]	[OH]+[HCO <sub>3</sub> ]+2[CO <sub>3</sub> ]	[+H <sup>-</sup> ]
4	1	1.00E-01	1.00E-13	1.00E-03	1.00E-03	4.47E-09	2.09E-18	1.00E-03	1.01E-01	4.47E-09	1.01E-01
5	2	1.00E-02	1.00E-12	1.00E-03	1.00E-03	4.47E-08	2.09E-16	1.00E-03	1.10E-02	4.47E-08	1.10E-02
6	3	1.00E-03	1.00E-11	1.00E-03	1.00E-03	4.47E-07	2.09E-14	1.00E-03	2.00E-03	4.47E-07	2.00E-03
7	4	1.00E-04	1.00E-10	1.00E-03	9.96E-04	4.45E-06	2.08E-12	1.00E-03	1.10E-03	4.45E-06	1.10E-03
8	5	1.00E-05	1E-09	0.001	9.57E-04	4.28E-05	2.00E-10	1.00E-03	1.01E-03	4.28E-05	9.67E-04
9	6	1.00E-06	1E-08	0.001	6.91E-04	3.09E-04	1.45E-08	1.00E-03	1.00E-03	3.09E-04	6.92E-04
10	7	1.00E-07	1E-07	0.001	1.83E-04	8.17E-04	3.82E-07	1.00E-03	1.00E-03	8.18E-04	1.82E-04
11	8	1.00E-08	0.000001	0.001	2.18E-05	9.74E-04	4.56E-06	1.00E-03	1.00E-03	9.84E-04	1.62E-05
12	8.1	7.94E-09	1.26E-06	0.001	1.74E-05	9.77E-04	5.76E-06	1.00E-03	1.00E-03	9.90E-04	1.04E-05
13	8.297	5.05E-09	1.98E-06	0.001	1.11E-05	9.80E-04	9.09E-06	1.00E-03	1.00E-03	1.00E-03	-6.94E-10
14	8.3	5.01E-09	2E-06	0.001	1.10E-05	9.80E-04	9.15E-06	1.00E-03	1.00E-03	1.00E-03	-1.54E-07
15	8.5	3.16E-09	3.16E-06	0.001	6.92E-06	9.79E-04	1.45E-05	1.00E-03	1.00E-03	1.01E-03	-1.07E-05
16	9	1.00E-09	0.00001	0.001	2.13E-06	9.53E-04	4.46E-05	1.00E-03	1.00E-03	1.05E-03	-5.25E-05
17	10	1.00E-10	0.0001	0.001	1.52E-07	6.81E-04	3.19E-04	1.00E-03	1.00E-03	1.42E-03	-4.19E-04
18	11	1.00E-11	0.001	0.001	3.94E-09	1.76E-04	8.24E-04	1.00E-03	1.00E-03	2.82E-03	-1.82E-03
19	12	1.00E-12	0.01	0.001	4.68E-11	2.09E-05	9.79E-04	1.00E-03	1.00E-03	1.20E-02	-1.10E-02
20	13	1.00E-13	0.1	0.001	4.77E-13	2.13E-06	9.98E-04	1.00E-03	1.00E-03	1.02E-01	-1.01E-01
21	14	1.00E-14	1	0.001	4.78E-15	2.14E-07	1.00E-03	1.00E-03	1.00E-03	1.00E+00	-1.00E+00

Figure 11. Spreadsheet with Calculations

Now we add HCl to lower the pH to 4.5 and determine how much HCl from the requirement that the moles of acid added produce a chloride concentration equal to the addition. We only need to change the charge neutrality calculation, and we force the pH value.

Thus the charge balance is

$$[H^+] + [Na^+] = [OH^-] + 2[CO_3^{2-}] + [HCO_3^-] + [Cl^-]$$

and the forced pH is 4.5. Now return the the spreadsheet and make the modifications and recompute.

	A	B	C	D	E	F	G	H	I	J	K	L
1	Closed Carbonate System - 1mM NaHCO3 - Add HCl to pH4.5											
2			[Na]	1.00E-03								
3	pH	[H <sup>+</sup> ]	[OH <sup>-</sup> ]	[Na]	[Cl]	[HCO <sub>3</sub> <sup>-</sup> ]	[HCO <sub>3</sub> ]	[CO <sub>3</sub> ]	[HCO <sub>3</sub> <sup>+</sup> ]+[HCO <sub>3</sub> ]+[CO <sub>3</sub> ]	[Na]+[H]	[OH]+[HCO <sub>3</sub> ]+2[CO <sub>3</sub> ]	[+H <sup>-</sup> ]
4	4.5	3.16E-05	3.16E-10	1.00E-03	1.02E-03	9.86E-04	1.39E-05	2.06E-11	1.00E-03	1.03E-03	1.03E-03	0.00E+00

Figure 12. Acid addition to pH = 4.5

Now to summarize the results.

Start with 1L water add 1 mM baking soda, pH = 8.3. Then add 1.02 mM of HCl, ph = 4.5.

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Now repeat the exercise with NaOH and HCl.

In this case we have only the water dissociation equilibrium, and charge

balance  $H_2O \Leftrightarrow H^+ + OH^-$   $K_w = [H^+][OH^-] = 1 \times 10^{-14} M$  Water Equilibrium

$[H^+] + [Na^+] = [OH^-] + [Cl^-]$  Charge Balance

In the first addition, the value of Cl is zero and the set the pH=4.5 We discover that we added  $2 \times 10^{-6}$  moles of NaOH (not much). Then when we added acid, the amount of HCl needed (from the knowledge that HCl is a strong acid) is  $3.4 \times 10^{-5}$  moles to get to pH 4.5

	A	B	C	D	E	F	G	H	I
2	Water + NaOH to pH = 8.3								
3									
4									
5	pH	[H <sup>+</sup> ]	[OH <sup>-</sup> ]	[Na]	[Cl]	[Na]+[H]	[OH]+[Cl]	[H <sup>+</sup> ]	
6	8.3	5.01E-09	2.00E-06	2.00E-06	0.00E+00	2.01E-06	2.00E-06	0.000000	Add NaOH
7	4.5	3.16E-05	3.16E-10	2.00E-06	3.40E-05	3.36E-05	3.40E-05	0.000000	Add HCl

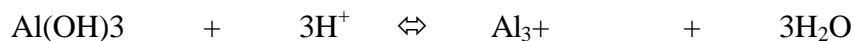
**Figure 13. Water without Buffer**

Buffered to go from pH 8.3 to 4.5 we added  $1.02 \times 10^{-3}$  moles acid. Unbuffered (same pH change) we added  $3.4 \times 10^{-5}$  moles acid. Nearly 96% less acid! Thus a buffered system needs more acid (orders of magnitude) to cause a change in pH than an unbuffered system. Natural mountain lakes are essentially unbuffered and for this reason acidic rainfall is especially damaging to the health of the species that live in these lakes.

At very low pH certain metals play an important role in buffering.



(kaolinite) => Aluminum ions (toxic)



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(gibbsite) => Aluminum ions (toxic)