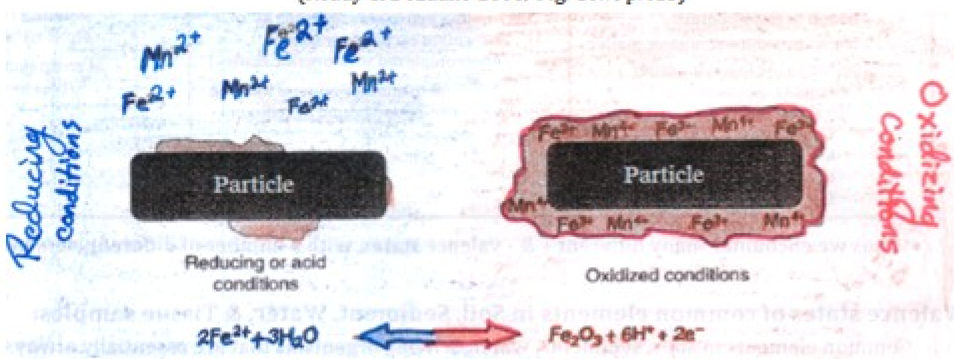
Special Importance of Fe & Mn Chemistry to Sediments & Wetlands

- **Oxidized vs. Reduced conditions:**
  - In upland soils, surface waters with dissolved oxygen, & in surface sediments of shallow water where **oxygen is present** (**oxidized** conditions), we tend to find **insoluble compounds** & **precipitates** of **oxidized Ferric** Iron (**Fe^{3+}**) & **Manganic** Manganese (**Mn^{4+}**).
  - In **Flooded**, wetland soils, where there's NO gaseous or dissolved Oxygen (**anaerobic**, or **anoxic**, or **reducing** conditions), we tend to find **soluble**, **reduced Ferrous** Iron (**Fe^{2+}**) & **Manganous** Manganese (**Mn^{2+}**).

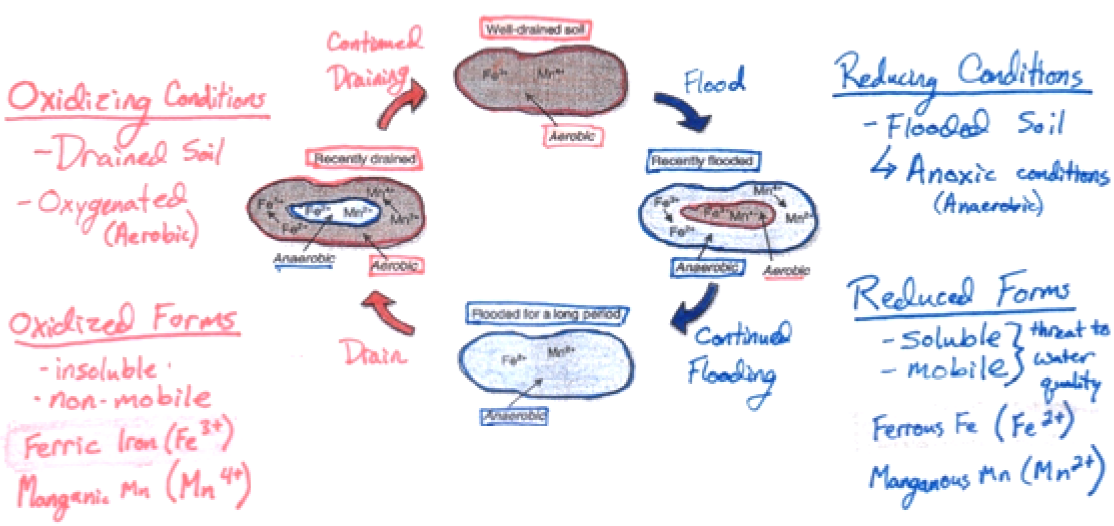
Portioning of iron & Manganese under reducing & oxidizing conditions
(Reddy & DeLaune 2008, Fig. 10.7, p.415)



- **These different valence states of Iron (Fe) & Manganese (Mn) are important because…**
  1) Plant & animal nutrition
  2) Toxicity to plants or animals
     - High concentrations of Iron (usually **reduced**) can be toxic
  3) Water quality
  4) Environmental chemistry of toxic elements
  5) Solubility & biological availability of many elements
     - The nutrient form of Phosphorous depends on the valence states of Iron

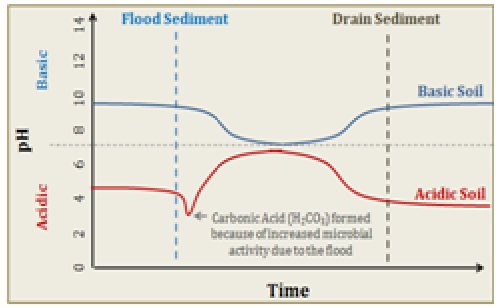
Oxidation-Reduction of Iron & Manganese under Flooded & Drained Soil Conditions

(Reddy & DeLaune 2008, Fig. 3.6, p. 49)



Why pH is important

- it is a factor affecting microbial activity in soils (what species are active & how active they are).
- pH affects the chemistry & availability of many plant nutrients & trace metals (phosphorous, iron, manganese, copper, zinc, etc.)
- pH affects the availability of many plant toxins, such as aluminum, iron, & manganese under some conditions
- pH affects the mobility (solubility) & plant availability of most toxic metals such as lead, cadmium, mercury, chromium, & others.
- pH of water is important to aquatic organisms for some of the reasons above (consider acid rain effects on poorly buffered lakes in the northeastern US, & acid mine drainage into streams & lakes in coal mining & metal mining areas).



pH Values of common substances & some natural materials

pH values of common substances & some natural materials

	pH	Substance
Very Basic	14	
	13	- Dilute sodium hydroxide (NaOH)
	12	- Lime water
Moderately Basic	11	- Household ammonia
		- "red Mud"
	10	- Milk of magnesia
	9	- Baking soda
	8	- Blood
		- Some coastal flooded marsh sediments
Neutral	7	- Pure water (exactly 7.0)
		- Many flooded soils & sediments (7.5 – 6.5)
		- Milk
Moderately Acidic	6	- Productive agricultural soils (5.5 – 8.0)
		- Tap water
	5	- Straight coffee
		- Tomatoes
		- Typical Rainfall (5.3)
	4	- Acid Rain (4.2)
	3	- Vinegar
		- Some oxidized fine-textured marsh sediments
		- Lemon juice
		- Wine
		- *Paedocypris progenetica* (an Indonesian fish)
Very Acidic	2	- Acid sulfate soils
		- Preserved water samples for metal analysis must have a pH<2 to keep the metals in solution
	1	- "Acid Fog" (1.7)
		- Stomach (gastric) fluids (1.7)
		- Dilute sulfuric acid
	< 0	- Strong acid solutions

(adapted from General College Chemistry 1961; Chemistry for Lab Technicians 1971; Manahan 2005, etc)

TABLE 14.3
H_3O^+ and OH^- Concentrations of Common Substances and the pH Scale

pH	$[H_3O^+]$	$[OH^-]$	pH *of Some Common Substances*	
−1	10	10^{-15}	Concentrated HCl (37%)	
0	1	10^{-14}	1*M* HCl solution	
1	10^{-1}	10^{-13}		
2	10^{-2}	10^{-12}	Stomach acid Lemon juice	Acid pH < 7
3	10^{-3}	10^{-11}	Orange juice Wine	
4	10^{-4}	10^{-10}	Soda water Tomato juice	
5	10^{-5}	10^{-9}	Rainwater	
6	10^{-6}	10^{-8}		
7	10^{-7}	10^{-7}	Milk	Neutral
8	10^{-8}	10^{-6}	Blood Seawater	
9	10^{-9}	10^{-5}	Baking soda solution Borax solution	
10	10^{-10}	10^{-4}	Toilet soap Milk of magnesia	
11	10^{-11}	10^{-3}		Basic pH > 7
12	10^{-12}	10^{-2}	Household ammonia	
13	10^{-13}	10^{-1}		
14	10^{-14}	1	1*M* NaOH solution	
15	10^{-15}	10	Drain cleaner	

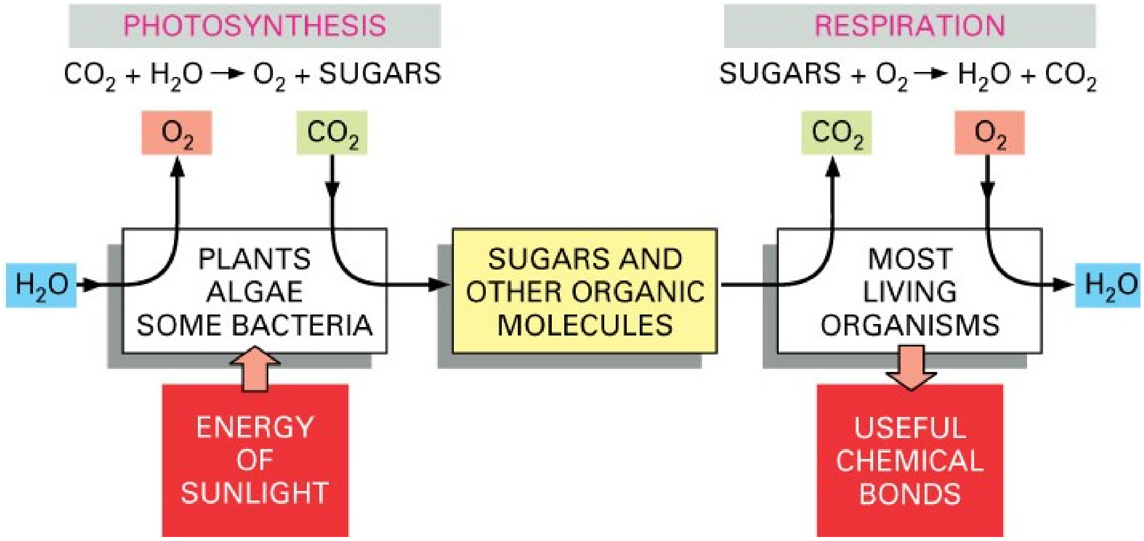
(Gillespie et al. 1989)

Acidic ↑ Neutral ↓ Basic

Environmental effects	pH value	Examples
	pH = 0	Battery acid
	pH = 1	Sulfuric acid
	pH = 2	Lemon juice, vinegar
	pH = 3	Orange juice, soda
All fish die (4.2 and below)	pH = 4	Acid rain (4.2–4.2) Acidic lake (4.5)
Salmon eggs (5.5 and below)	pH = 5	Bananas (5.0–5.3) Clean rain (5.6)
	pH = 6	Healthy lake (6.5) Milk (6.5–6.8)
	pH = 7	Pure water
Calcifying marine organisms begin to dissolve (8.0 and below)	pH = 8	Healthy ocean (8.2)
	pH = 9	Baking soda
	pH = 10	Milk of magnesia
	pH = 11	Ammonia
	pH = 12	Soapy water
	pH = 13	Bleach
	pH = 14	Liquid drain cleaner

(Chamberlin & Dickey 2008)

Chemical Oceanography Review



1) **Photosynthesis**

- Using energy from the sun to convert carbon dioxide & water into **carbohydrates** (organic matter)
- This reaction stores energy as plant material (& subsequently as organic matter found in soils & sediments & in some situations, eventually getting to oil, gas, & coal deposits.
- Photosynthesis results in the storage of light energy as chemical energy in plants.

$$\underset{\text{Carbon Dioxide}}{6\,CO_2} + \underset{\text{water}}{6\,H_2O} \xrightarrow{\text{sun}} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{oxygen}}{6\,O_2}$$

- This reaction results in the storage of 686 kilocalories/mole of glucose (1 mole of glucose is 177 grams)
- This energy can be released during respiration by organisms ranging from bacteria to mammals.
- *Note*: Glucose is a carbohydrate or a simple sugar produced by plants.
  - └ Though certainly not all plant organic matter is glucose, we are going to consider glucose as a model organic compound for comparing energy yields in various respiration reactions.

2) **Respiration**

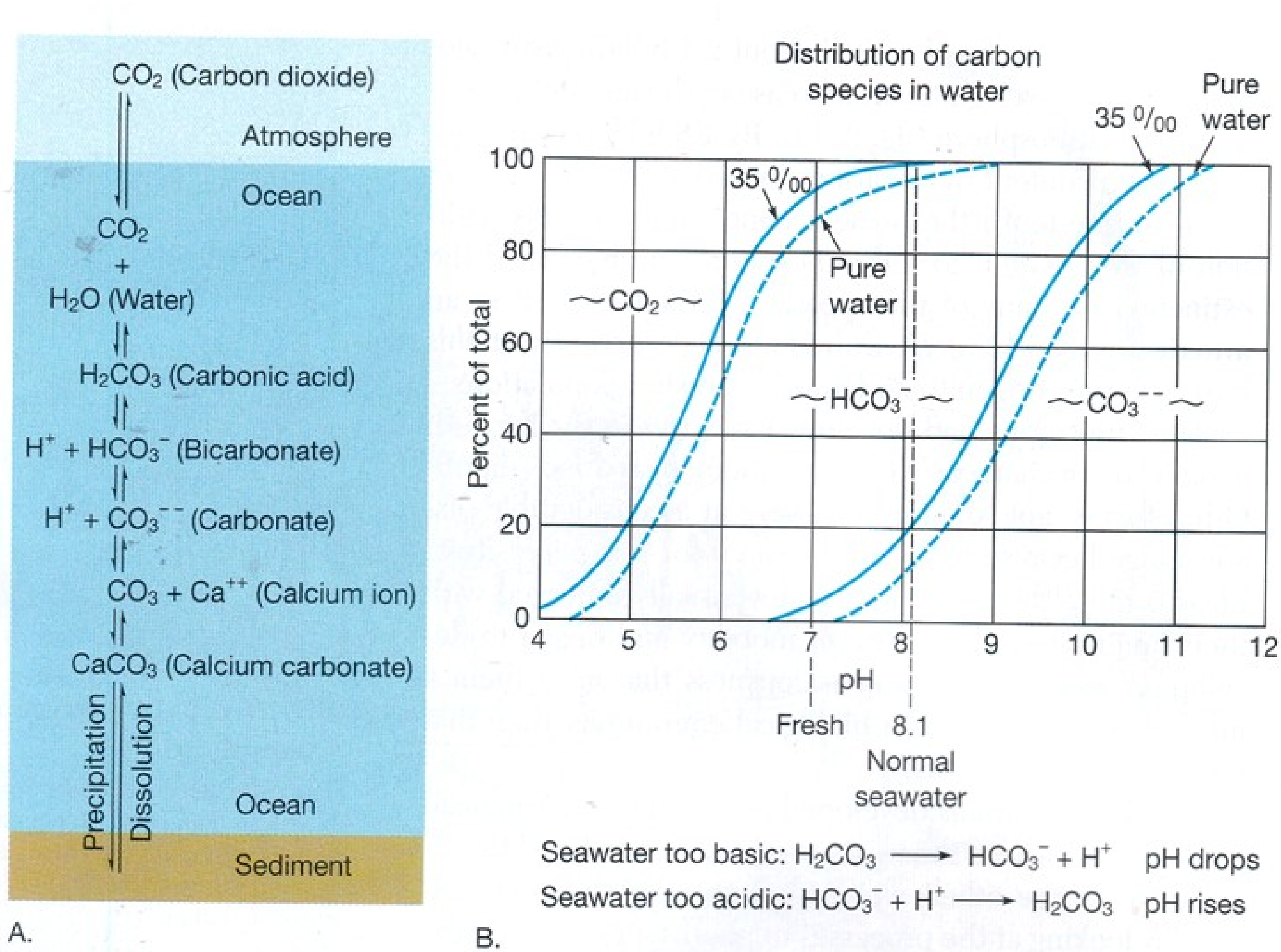
- the derivation of energy from organic matter produced by photosynthesis.
- This energy is derived from organic matter by microorganisms & animals.
- Combustion or fire would be a non-biological reaction that would derive about the same amount of energy from organic matter as aerobic respiration, but, we'll stick with respiration as the demand for organic matter as an energy source.
- The **reverse reaction**, the **biological release of the energy by oxidation of this carbohydrate** back into its original constituent components, is called respiration.
- The energy derived from this oxidation is used by various organisms ranging from bacteria to mammals

$$\underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{oxygen}}{6\,O_2} \Longrightarrow \underset{\text{carbon dioxide}}{6\,CO_2} + \underset{\text{water}}{6\,H_2O} + \underset{\text{energy}}{\text{Energy}}$$

- The actual reaction is a **two-part reaction:** (i) the **oxidation of glucose** & (ii) the **reduction of oxygen.**

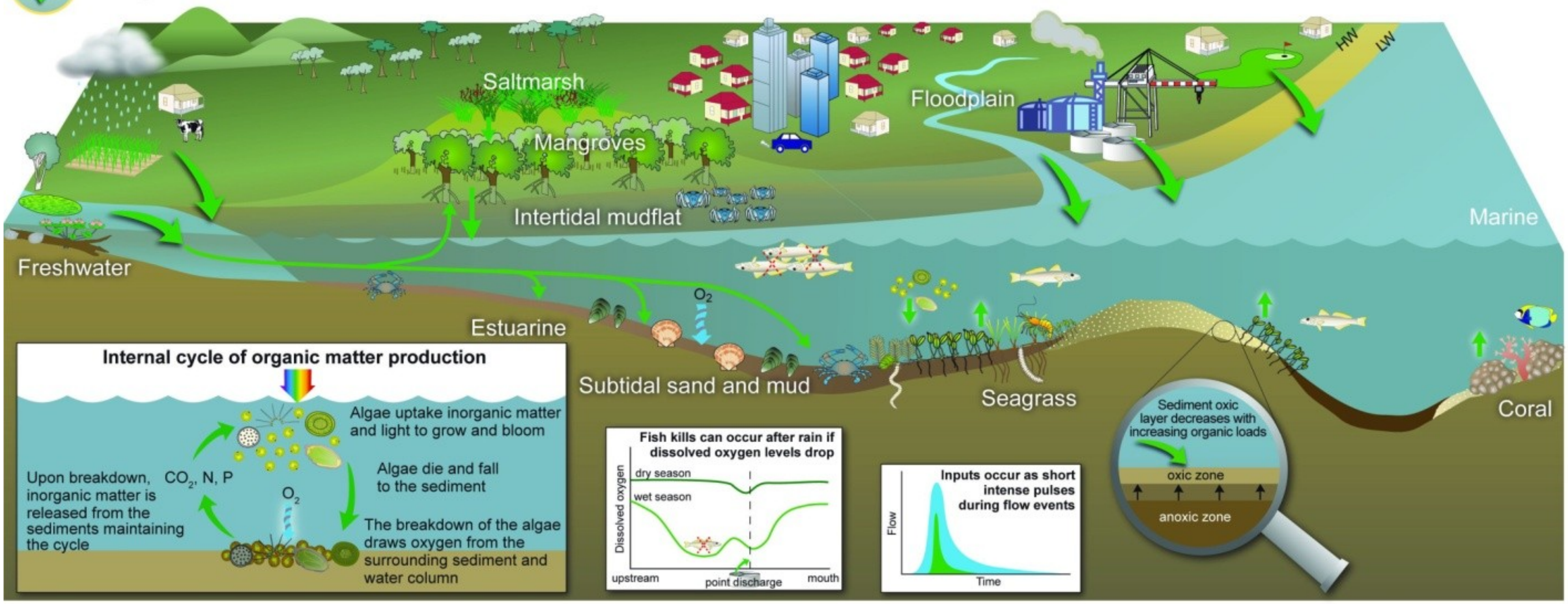
FIGURE 2–13 Carbon Species and the Marine CO_2 System.

A, the CO_2 system. Atmospheric carbon dioxide diffuses into the ocean, combines with water, and produces carbonic acid. The carbonic acid dissociates into bicarbonate and hydrogen ions. Some bicarbonate dissociates into carbonate ions, which combine with calcium ions to form calcium carbonate. *B*, at the normal pH of ocean water, 8.1, more than 80% of the carbon in ocean water is in the form of bicarbonate (HCO^-_3). If the pH rises, the reaction shown in part A moves upward. This releases more H^+ into the water and lowers the pH. If the pH drops, the reaction moves downward, removing H^+ from the water and causing the pH to rise. Thus, the pH of ocean water varies little from a value of 8.1.



Nitrogen (N) Chemistry

Organic matter



Legend:

Organic matter enters from diffuse land ( ), urban ( ) (e.g. stormwater), upstream aquatic (e.g. aquatic weeds ( )) and point discharge ( ) (e.g. sewage overflow and intensive animal production (e.g. dairy, feed lot)) sources

Internal production of organic matter from aquatic plants ( ) and phytoplankton ( ) occurs within the system

The breakdown of organic matter can result in low dissolved oxygen (i.e. hypoxia or anoxia) in the water which can cause mass mortality events

Sediment oxygen demand is higher when production is higher

Queensland Government
Environmental Protection Agency