Importance of Phosphorous

General Information

- **Phosphorous (P) is a major nutrient, essential for plant & animal nutrition**
  - P is often limiting in agricultural soils
    - is commonly applied as a **fertilizer** application annually for agricultural crop production
      - because once P has been out of the soil for a while, it tends to change into more unavailable forms)
  - P is rarely limiting plant growth in wetland systems
  - It is often added to animal feeds as a nutrient supplement in major livestock operations where the animals are fed prepared feeds instead of grazing (such as operations growing chickens & pigs, & sometimes cattle in confinement)
- **Excess P in surface waters (such as lakes & bays) may contribute to undesirable water quality**
  - **Algae blooms**
  - **Eutrophication**
    - > 0.02 mg P/L said to be associated with freshwater eutrophication
    - total P > 0.1 mg P/L is too high for most surface waters
      - 0.02 mg P/L causes problems in some water

Changes that occur when freshwaters become Eutrophic

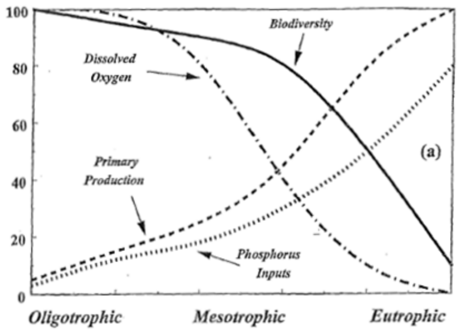


Fig. 5.1a, Pierzynski et al. 2000, adapted from Correll 1998

As a system gains more P, growth rates ↑ → ↑ Primary Production → ↑ Production uses ↑ Dissolved O_2 (DO) → ↓ available DO → ↓ Biodiversity

Boundaries for Trophic Status of Water Bodies
(ie. concentrations of P found in different degrees of polluted water bodies)

Oligotrophic system	< **10** microgram total phosphorous per liter
Mesotrophic system	10 – 35 microgram total phosphorous per liter
Eutrophic system	**35-100** microgram total phosphorous per liter
Hypereutrophic	>100 microgram total phosphorous per liter

- **Limiting Nutrients for Eutrophication Aquatic Systems**
  - **Phosphorus** is limiting for **freshwaters**
  - **Nitrogen** is often the limiting for **coastal waters**
- **Sources** of **P** to **surface waters** includes both **point** & **non-point sources**
- The **P cycle** is unique because it has **no significant transformation** & **transport** through a **gas phase**
- P movement through the atmosphere adsorbed to dust particles & sea spray (1.0×10^{12} g/yr) is also less than for other major element transport by this route, but, this is significant in areas where P is very limiting.
- **Microbial processes are <u>not important</u> in making available original sources of phosphorous (weathering of phosphate minerals) unlike occurs for natural for natural sources of available**
- The **primary, most abundant mineral source of P** is the **calcium phosphate mineral, Apatite [$Ca_5(PO_4)_3OH$]**
- **Phosphate content** of **most rocks & the total P** in **most soils is low**
  - only a small % is biologically available
  - Thus **recycling** & especially the **rate of recycling** of P between **organic** (living matter, detritus, & humic material) & **plant available mineral forms** is **important** to the **availability of phosphorous.**
  - **Microbial processes** are **important** in the **transformation** between **available inorganic** & soil/sediment **organic P.**
- **Rivers** are the **main transport process** for moving **P to the** Oceans (21×10^{12} g/yr)
  - In the oceans ~ **10%** is **available** for **marine biota** & **90%** remains **bound to eroding soil particles** that settle to the continental shelf & become bound with sediments.
- The **turnover time** for **organic P** in **surface ocean waters** is **rapid** (days)
  - most is in phytoplankton that dies where the organic P is remineralized to become available inorganic P again

Adverse Environmental Impact

- **its role in eutrophication**
  - **Eutrofication is** the excess P, N, & adequate availability of other essential nutrients cause the algal population to become so large that the microbes are able to consume most or all of the dissolved oxygen in water

❖ Forms of Phosphorous

Changes in the form of soil Phosphorous (P) as affected by time & soil development for total P

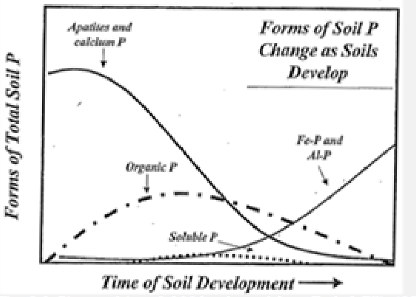


Fig. 5.5, Pierzynski et al. 2000, adapted from Foth & Ellis '97

- ○ Most Soils & Sediments contain both organic & inorganic forms of P (just like they do with N & S)
- ○ There is considerably **more variability** in amounts of **organic vs. inorganic P** in soils/sediments **than there is with nitrogen**
- ○ **Relationship between 2 & 4 (as Fe becomes unstable P will go from 4 to 2)**

1) **Organic** Phosphorous

- **Organic P is not available** (just like with N & S)
  - └ though there is recently more debate concerning soluble, organic P compounds being passively taken up by plants & then the phosphorous is released to mineral (inorganic) form by enzymes in the plant
- Organic P **becomes available** through **mineralization of organic matter** (just like with N & S)
  - somewhat like N & S (except in highly pyritic sediments),
- Organic P is often a **large proportion** of the **total** in **soils & typical fine-textured**, **high humic material** sediments, but it can be a small part of the total in some soils (Evangelous 1998)

2) **Inorganic, Soluble** ("Available") Phosphorous

- ○ **Forms:** PO_4^{3-}, HPO_4^{2-}, & $H_2PO_4^-$ (Which of these forms predominates depends mostly on pH ?)
  - these forms exist in equilibrium with insoluble P forms such that only a small amount may be in the soluble, available forms at any time.

Unavailable		**Available, Soluble**
Organic Phosphorous	← microbial activity →	$H_2PO_4^-$
Insoluble, inorganic Phosphorous	← chemical transformations → Influences by microbial activity (redox changes)	$H_2PO_4^-$

- ○ **Mobility**
  - soluble P compounds move **more slowly in water** moving through a soil & would not keep up with Cl^- & NO_3^-
    - └ Whereas Cl^- & NO_3^- are not retained with soil (except at unusually low pHs) & move readily with water
  - **Phosphate** is **retained more strongly** by **sorption processes**
    - though some of the adsorbed forms are in ready equilibrium with soluble P
    - So, to have soluble P, there are equilibrium reactions that release some to solution, but maintain most as insoluble forms
  - As a general rule, **significant P does not leach** (move downward in soluble forms with rainwater) in upland soils that are fine textured (silt & clay & soils with appreciable amounts of reactive iron, calcium, or aluminum).

The pH distribution of the phosphate series

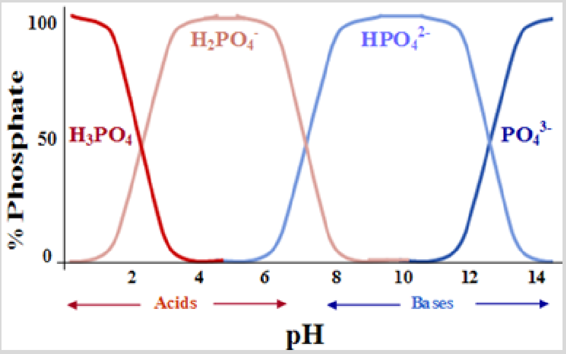
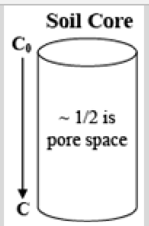


Fig. 11.1, Bohn et al. 1985

- pH is what determines which form of Phosphorous will be present
  note: all of these forms of Phosphorous are soluble

Representative breakthrough curves of anions weakly, moderately, & strongly retained by soils



C/C_0 = changes in concentration of some solution poured through a soil core; where C_0 is the initial Concentration

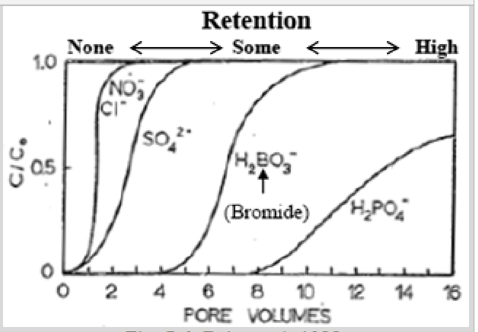


Fig. 7.6, Bohn et al. 1985

- In soils & sediments some anions are retained more than others
- Cloride (Cl^-) & Nitrate (NO_3^-) are NOT retained b/c they're too mobile
- Cl^- can be used as a tracer for NO_3^-, thus if NO_3^- dissapears & Cl^- doesn't, than NO3- hasn't been absorbed but rather has changed into something else (Bromide can also be used as a tracer for NO_3^-)
- Inorganic P is not nearly as mobile in Soils & Sediments
- $H_2PO_4^-$ is the most common form of Phosphorous in neutral pH

3) Inorganic Compounds containing Phosphorous

Chemical "Forms" that should be considered as Classes of Compounds

- **Al-PO$_4$**, tightly bound, **insoluble**, especially in moderately acid soils (extreme acidity would make this form available, but extreme acidity is normally not achieved in soils, wetland soils & sediments)
- **Fe-PO$_4$**, tightly bound, **insoluble**, especially in acid soils (extreme acidity would make this form available, but…)
- **Ca-PO$_4$**, many forms, but solubility tends to ↓ with ↑ pH (**very insoluble at high pH**, more soluble under acid conditions, but, fairly rapidly would dissolve & leach out of acid soils, so, acid soils don't have a lot of this form
- **PO$_4$** can also precipitate on CaCO$_3$, in alkaline soils

Solubility of Calcium phosphates compared to Strengite (Fe(OH)$_2$H$_2$PO$_4$) & Variscite (Al(OH)$_2$H$_2$PO$_4$), when Ca^{2+} is 10$^{-2.5}$ M or fixed by Calcite (CaCO$_3$) & Carbon Dioxide (CO$_2$) at 0.0003 atm

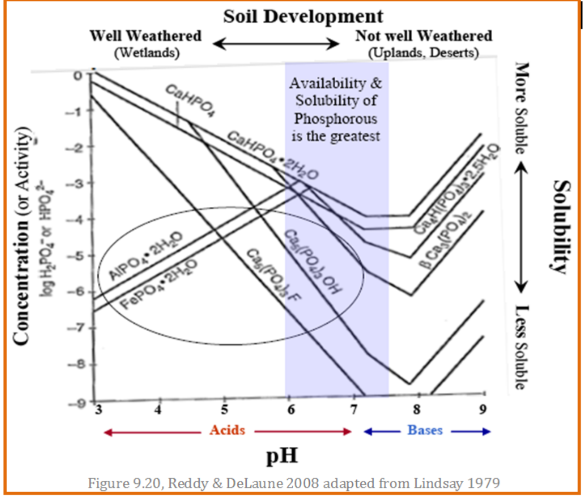
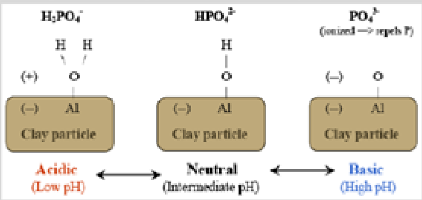


Figure 9.20, Reddy & DeLaune 2008 adapted from Lindsay 1979

Solubility of Phosphorous compounds & soil pH

- These general forms tend to limit solubility where the major cations are abundant & pH is as indicated
- P **solubility** & **availability** tends to be the **greatest** at **near neutral pH levels (6–7.5)**, because…
  - the **unusual abundance** of **reactive Al & Fe in acid** (low pH) soils, but not in basic (high pH) soils
  - the **usual abundance of Ca in basic soils** but limited in acid soils
  - P availability ↓ as the soils become more acidic or more basic
- In acid soils, much of the P is **Al-PO$_4$**, very insoluble, but with time, it may become ferric phosphates (**Fe-PO$_4$**) which is less soluble
- As you go up the log H$_2$PO$_4^-$ scale, solubility of the compounds ↓ (ie. max solubility of P is near pH 5-6)
- Soils above pH 7 are generally less developed (less "weathered") with abundant Ca & all the compounds sloping down are calcium phosphate compounds
- As soils develop (& "weather" more rapidly in hot, high rainfall climates over hundreds to thousands of years), the Ca gradually leaches out & there is more chemically reactive iron & aluminum (Fe & Al) & pH drops.
- As the pH ↑ above 7, calcium phosphates form, & as it ↑ above 8, they become increasingly **less** available
- As the pH ↓ & becomes more acidic it forms Al & Fe phosphates which are generally insoluble
  - └ this is the opposite of most metals which generally become more soluble as pH ↓ & becomes more acidic
- Variscite (Al(OH)$_2$H$_2$PO$_4$) & Strengite (Fe(OH)$_2$H$_2$PO$_4$) are Fe & Al phosphate compounds
- Thus in **flooded sediments** the concentrations of **soluble P & dissolved Fe** ↑; whereas, in **oxidized** environments (ie. surface waters) there's very **little soluble P or dissolved Fe**, this is because these forms will react with the forms in the beneath zone & precipitate out
- A lower value of pH$_2$PO$_4$ indicates greater solubility

Schematic showing the influence of pH on positive or negative changes on Aluminum (Al) solid phase



Adapted from: Figure 9.19, Reddy & DeLaune 2008

Representation of H$_2$PO$_4^-$ penetration into an iron oxide surface & subsequent formation of a stable binuclear bridge

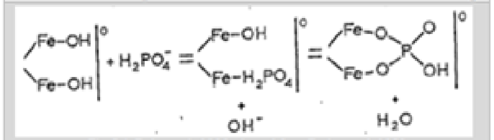
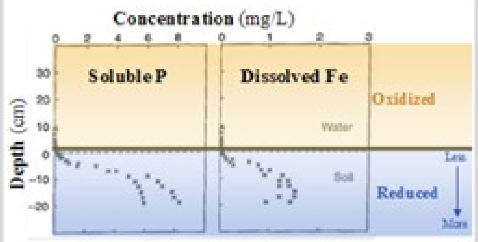


Fig 7.4, Bohn et al. 1985 adapted from Ryden et al. 1973

4) Reductant Soluble Phosphate

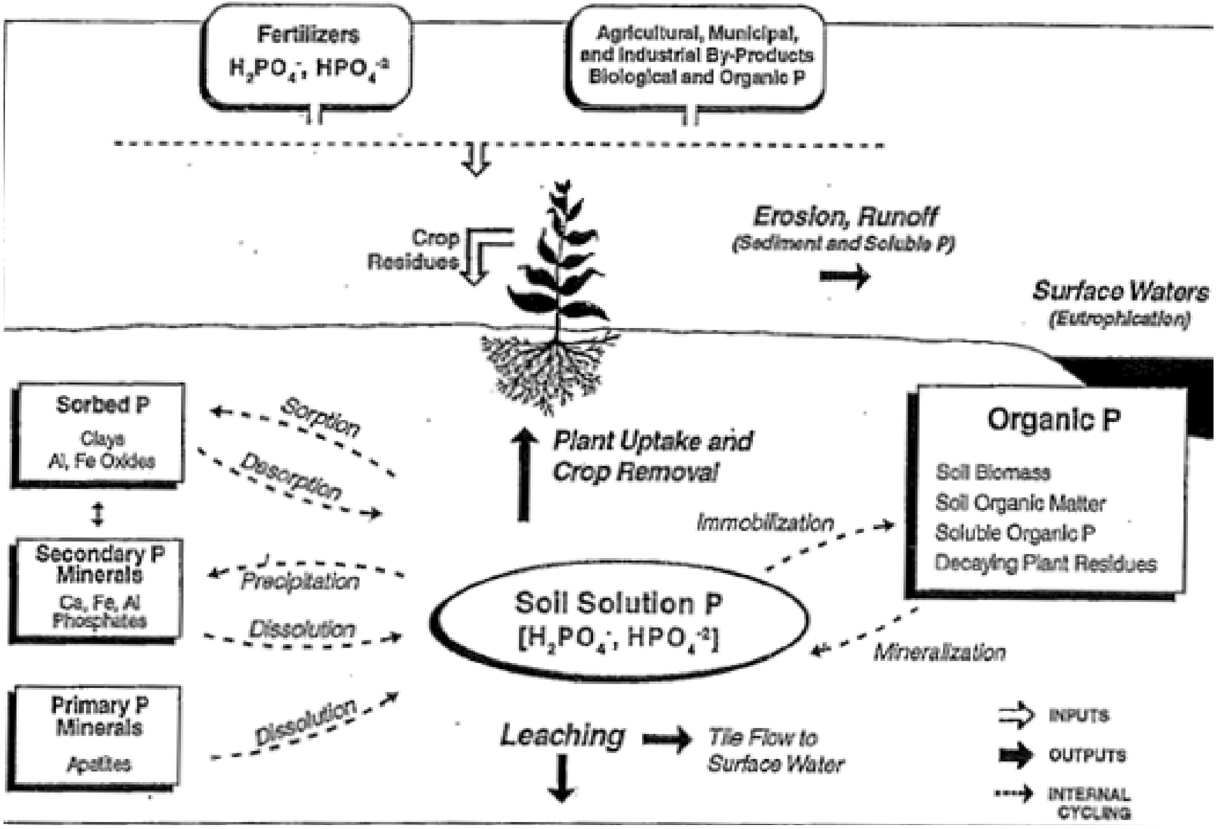
- Phosphate as PO$_4^{3-}$, HPO$_4^{2-}$, & H$_2$PO$_4^-$, & even P compounds like the Al-, Fe-, & Ca-P compounds mentioned above can be "occluded" by precipitated ferric iron oxyhydroxides (an amorphous, colloidal, iron oxideliron hydroxide polymer sometimes represented by FeOOH).
  - └ "**Occluded**" means bound within the matrix of a solid particulate of compounds like ferric iron oxyhydroxides.
- In **oxidized** soils, amorphous ferric oxyhydroxides form, are stable, & trap & hold phosphate compounds.
  - └ However, if a soil becomes **flooded & goes reducing**, **insoluble ferric (Fe^{3+})** compounds **become more soluble ferrous (Fe^{2+})** compounds, releasing P to more soluble & available forms
- This is why P is often limiting for plant growth in upland soils, & is rarely limiting in wetland soils.
- This form of P in oxidized soils is measured by extracting soil with a strong chemical reducing agent that reduces the iron

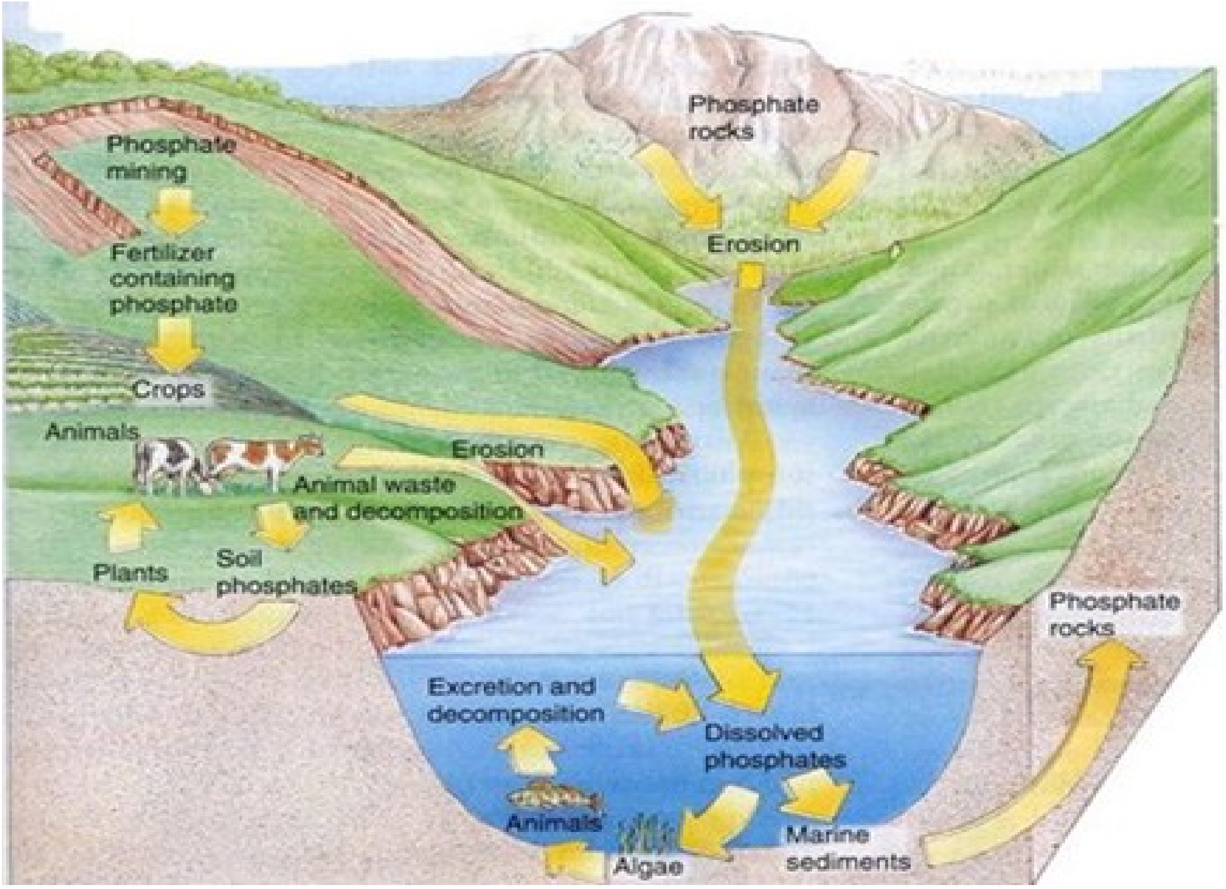
Soluble Phosphorous & Dissolved Iron profiles in wetland soil showing the relationship between Iron Reduction & Phosphorous Release



Adapted from: Figure 9.56, Reddy & DeLaune 2008

❖ Phosphorous Cycle





Phosphorous (P) Chemistry

➢ Processes involved in Phosphorous Release after Flooding & Soil Reduction

- **Hydrolysis of ferric & aluminum phosphate: $FePO_4 + H_2O \rightarrow Fe(OH)_2 + H_2PO_4^-$**
  (depending on pH, not much P may be released by this process)

- **Release of P adsorbed to clays & surface adsorbed to iron oxyhydroxide particulates or coatings by anion exchange processes**
  - recall the anion bicarbonate forming in appreciable amounts upon flooding ($H_2O + CO_2 \rightarrow H^+ + HCO_3^-$) then eventually more OH^- forms as pH begins to increase upon flooding a moderately acid soil.

- **Reduction of ferric compounds containing phosphate to more soluble ferrous compounds**
  - Insoluble ferric →(reduction)→ more soluble ferrous phosphate compounds iron & phosphate (remember, these ferric phosphate compounds get less soluble as pH decreases in oxidized systems)

- **Release of phosphate occluded or adsorbed to large molecular weight iron oxides**
  (not specific compounds, this is the "reductant soluble phosphate" mentioned earlier)
  - In **oxidized soils**, except for strongly acid conditions, these iron oxides & hydroxides are **very insoluble** & **very stable**
  - these iron oxides & ferric oxyhydroxide particulates & coatings get unstable & more soluble as pH & redox potential ↓

Near Neutral pH & Oxidizing Conditions	⇔	**Acid Conditions &/or Reducing Conditions**
Solid iron oxides & oxyhydroxides bind P tightly		Solid iron becomes unstable & dissolves, releasing P to soluble form

★ Under **reducing** soil conditions, some of these **insoluble ferric** [phosphate] compounds are transformed to the **more soluble ferrous** compounds **releasing phosphorus in the process.**

- this is **a major source** of **soluble & available P under reducing conditions**
- Studies have shown that when a **soil is flooded** & **redox potential is ↓,** the potential at which dissolved iron levels show a marked ↑ is where soluble levels of phosphorus ↑ also.
- Recall the 2 lake systems : Unstratified Reservoir (Oxidized water column with oxidized sediment layer) vs. Stratified Resevoir (oxidized surface water layer, anoxic (reduced) subsurface water layer with completely anaerobic sediment)

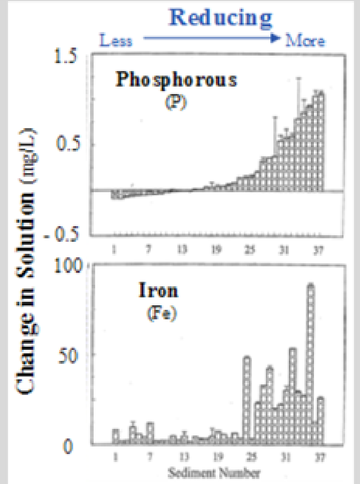
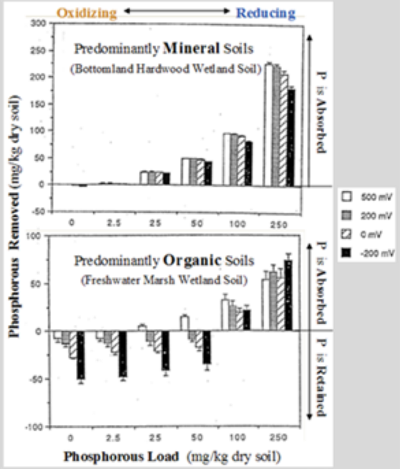
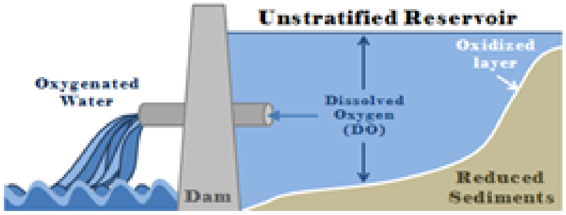


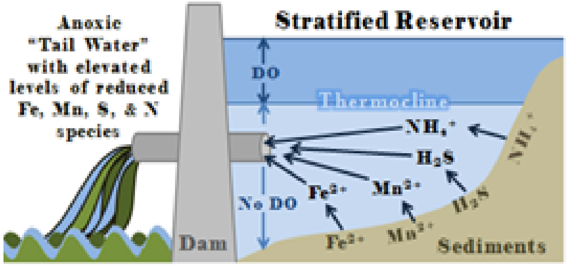
Fig. 5.15 Pierzynski et al. 2000, adapted from Sallade & Sims 1997

Phosphorus Release, & Removal Capacity as Affected by Soil Redox Status & P Loading Rate



Adapted from: Figures 1 & 5, Masscheleyn et al. 1992





➢ Environmental Chemistry of Phosphorous

Redox Conditions

- Under very **strongly reducing** conditions there is a (-3) valence for P generating some phosphine gas (PH_3)
- most P is generally **not subject to valance state changes** in soils & plants that affects its chemistry as are N, Fe, & S
  - └ all 3 of the **inorganic species** of P have a valence state of +5, & **differences** between them are **due solely to changes in pH**
  - └ changes in **redox potential** & **pH** → **chemical changes** affecting **P solubility** & **availability**, but **NOT** its **removal** from **soil** (unlike Nitrogen, which is removed from soils by redox potential influences transformation processes, like Dinitrification, where the soluble Nitrate is converted to Nitrogen gas & returned to the atmosphere)
- Soil & sediment redox & pH conditions greatly affect the solubility & availability of P, but not its removal

Importance of Sulfur

- a **major terminal electron acceptor** in **strongly reduced** coastal sediments
- important in **energy transport** in salt marshes
- important to environmental chemistry of **trace** & **toxic metals** (especially in contaminated coastal sediments)
- understanding the biogeochemistry of sulfur has enormous economic impacts (metal ores, adverse SO_2 impacts from burning coal & oil, smelting copper ore)

Favorable Environmental Impacts of Sulfur

- **an Essential Plant Nutrient**
  - However, it is rarely limiting & our interest in sulfur focuses on other roles it plays in soils & sediments

Adverse Environmental Impacts of Sulfur

Sulfur Toxicity

- **To Plants**
  - An important plant toxin or stress factor in some salt marshes
  - some industrial sulfur emissions impact vegetation for great distances
- **To Animals**
  - Both ruminant & non-ruminant animals can suffer from S toxicity
  - ruminants are susceptible to excess S in the forms of $(NH_4)_2SO_4$ & gypsum ($CaSO_4$) when these are used as nonprotein N or Ca feed sources, respectively
  - non-ruminants are susceptible to excessive S amino acids, especially methionine, in their diet
  - livestock are also sensitive to H_2S
- **To Humans**
  - Sulfur as a Nuissance, or as a Threat to Human Health
  - See Hydrogen Sulfide (H_2S) section

Acid-Related

- **Acidic Deposition**
  - contributes to acid rain
  - Sulfuric acid ($\mathbf{H_2SO_4}$) formation in the atmosphere results in wet (rain, snow, fog) & dry deposition (particulates) may be detrimental to vegetation, surface waters, buildings & structures, & humans
- **Acidic Sulfate Soils**
  - Caused by the release of $\mathbf{H_2SO_4}$ into the soil solution through the oxidation of sulfidic materials that are commonly associated with coastal regions & lignite coal mining operations
- **Acid Mine Drainage**
  - Oxidation of reduced forms of S from mining activities produces H_2SO_4 that can impact the soils or mine spoils & surface waters in the surrounding environments

Geothermal Activity

- Geysers & other geothermal releases can bring significant amounts of gaseous & soluble S compounds to the earth's surface
- vegetation in the surrounding area can be killed by S gases or the extremely acidic soils that form
- soil pH values as low as 0.9 have been reported in Yellowstone National Park, WY

Groundwater Contamination

- High SO_4 concentrations can render groundwaters unsafe for human & livestock consumption

Forms of Sulfur

General Forms of Sulfur in the Environment

Organic Forms

- Organic S in living plant, animal, & microbial tissue (as essential components of amino acids & proteins)
- Organic S primarily in soil & sediments as **humic material** (naturally occurring soil & sediment organic matter)

Inorganic Forms

- Inorganic sulfur compounds in the **atmosphere** (sulfur dioxide, SO_2, & others)
- Inorganic forms in upland **oxidized** soils & surface waters (sulfate, SO_4^{2-}, is the primary compound) Seawater contains about 885 mg/L (ppm) of sulfate-sulfur & sodium sulfate, $NaSO^4$
- Inorganic forms in **strongly reduced** sediment & water environments (elemental sulfur, S^0, & Sulfide S^{2-})

Inorganic Forms of Sulfur in Soils & Sediments

Mean Oxidation States			
Sulfides	Sulfur	Sulfites	Sulfates
- 2	0	+ 4	+ 6

Sulfate (SO_4^{2-})

- an important oxidized inorganic form
- it's soluble, non- toxic, & very abundant in seawater (Seawater is ~885 ppm Sulfate)

Sulfide (S^{2-})

- at normal pH levels, as soon as it's formed, it either becomes hydrogen sulfide (H_2S), or a metal sulfide precipitate (such as FeS). (See next two entries for an introduction to these forms)

Hydrogen Sulfide (H_2S)

- It is relatively soluble & it is a gas
- In some wetlands, its toxicity to plants is usually more of a stress factor than outright acute toxicity.

Pyrite (FeS_2)

- an inert solid precipitate under strongly reduced conditions
- Pyrite can sometimes cause some serious pH problems when it is exposed to oxidized conditions

Elemental Sulfur (S^0)

- important reduced form, its reduction status is between that of sulfate (S^{6+}) & sulfide (S^{2-}).

(S^{2-} & H_2S react quickly with most divalent metals (Fe^{2+} or Cu^{2+}) forming insoluble precipitates important to trace & toxic metals)

Forms of Sulfur in Coastal Salt Marsh Soil

Acid Volatile Sulfides (AVS)

- Sulfide that will become volatile if acid is added
- Dissolved H2S & HS- & iron monosulfide (FeS)

HCl-soluble S

- pore water sulfate (SO_4^{2-}), thiosulfate ($S_2O_3^{2-}$), polythionates, polysulfides (Sn^{2-}), soluble organic S, & HCI-hydrolysable organic S (sulfate polysaccharides & amino acids).

Pyrite S

- pyrite & marcasite (FeS_2)

Elemental S (S^0)

- Can often be seen as a white plume coming out of small permanently flooded channels in salt & brackish marshes, & sometimes from the surface of a tidally flooded marsh.

Ester-Sulfate S

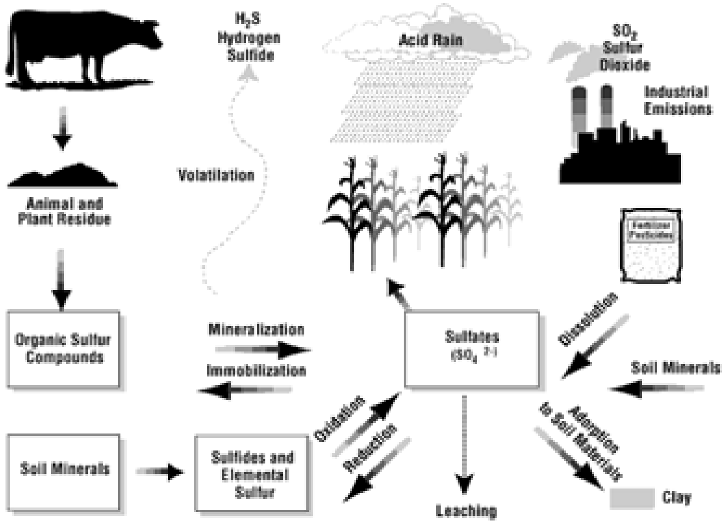
- organic S not directly bonded to C, Ester sulfates (-C-0-S-), sulfamic acid (-C-N-S-), & S-sulfocysteine (C-S-S-)

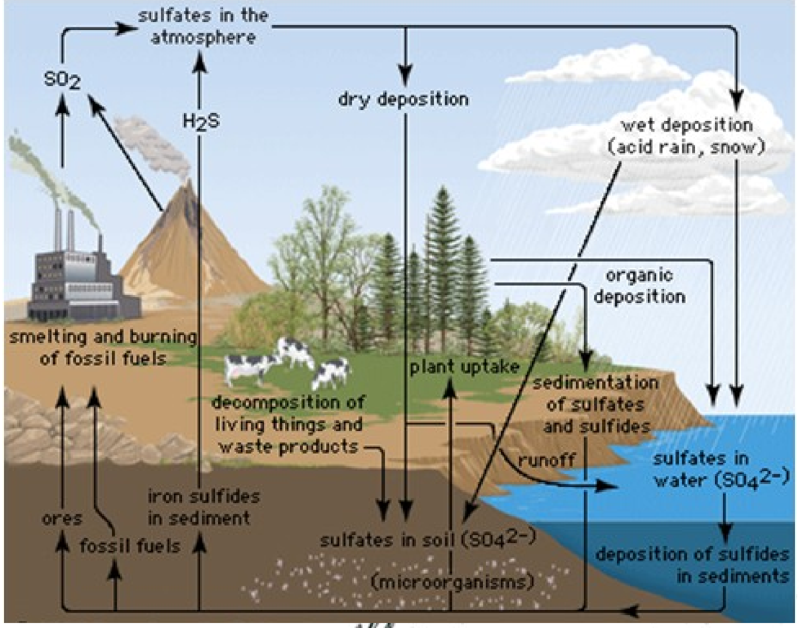
Carbon-based S

- organic S directly bonded to C, peptides, proteins, coenzyme, sulfolipids, aliphatic sulfones, sulfonic acids, (methionine sulfone, & cysteic acid) & heterocyclics)

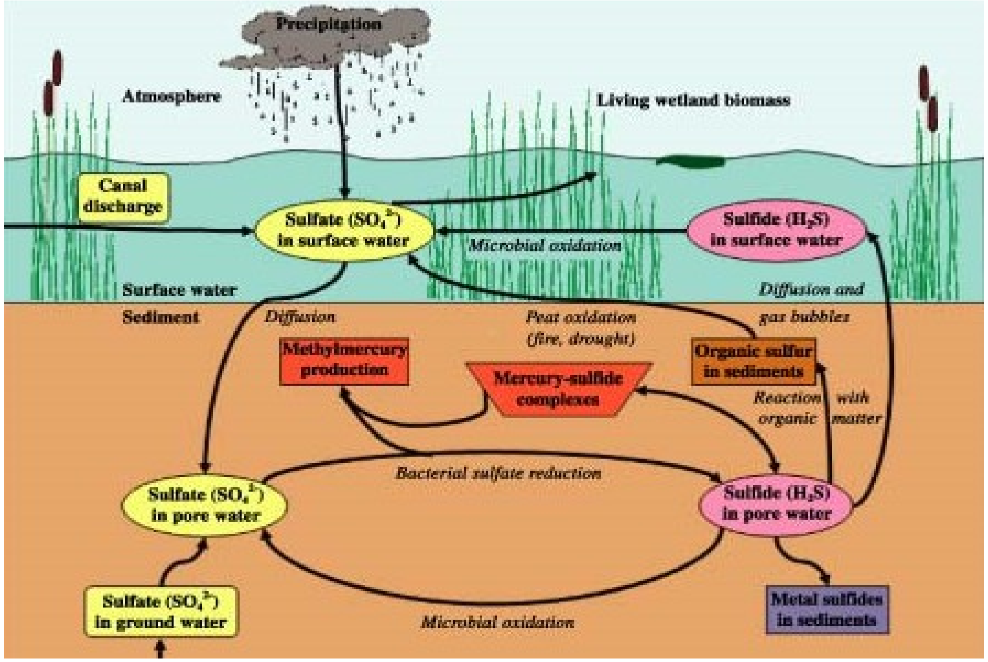
Sulfur (S) Chemistry

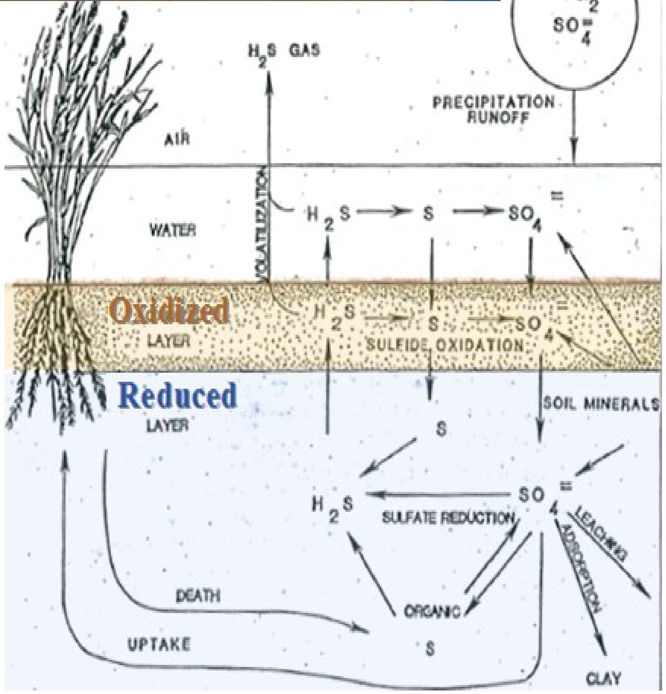
❖ Sulfur Cycle



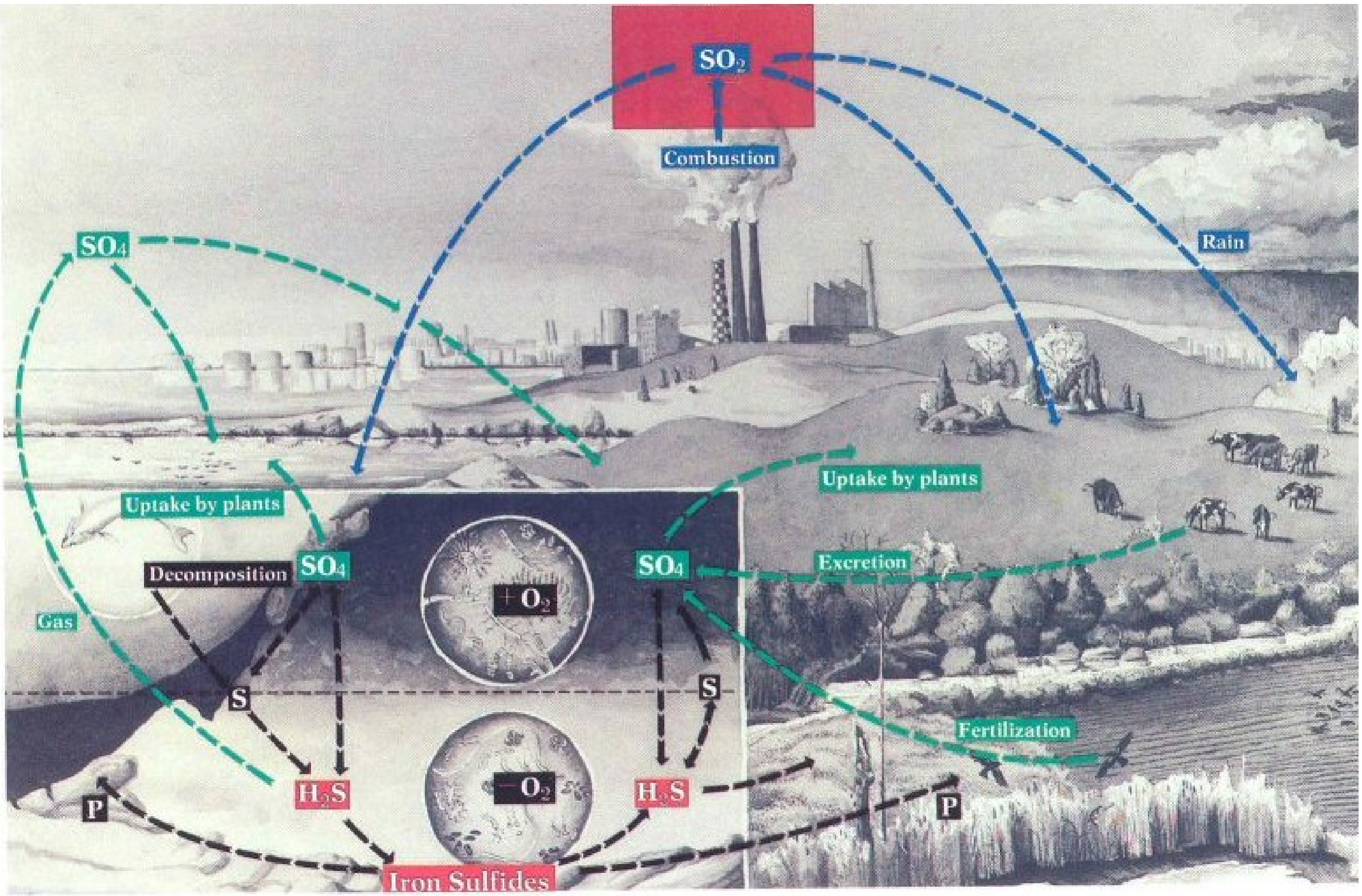


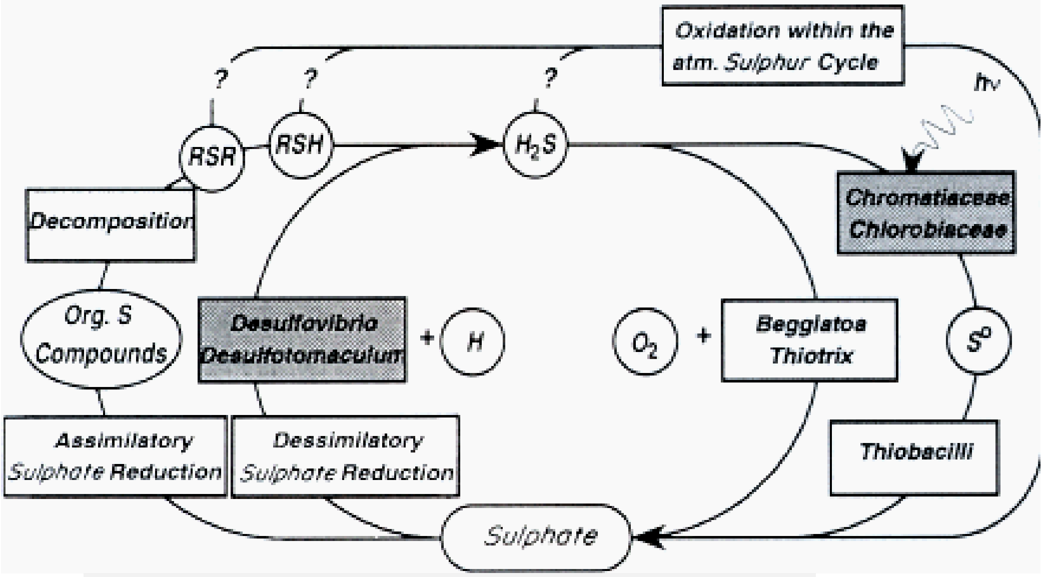
➢ Sulfur Transformations





Sulfur (S) Chemistry





$8\,[H] + SO_4^{2-} \rightarrow H_2S + 2\,H_2O + 2\,OH^-$	anaerobic	▨
$2\,CO_2 + H_2S + 2\,OH^- \xrightarrow{h\nu} 2 < CH_2O > + SO_4^{2-}$	anaerobic, photothropic	hν ▨
$2\,H_2S + O_2 \rightarrow 2\,H_2O + 2\,S$	aerobic	□
$S + H_2O + 1½\,O_2 \rightarrow SO_4^{2-} + 2\,H^+$	aerobic	□

Sources of Sulfur

Natural

- Sulfur is a **ubiquitous** element
  - Atmosphere
  - Minerals, Soils & Sediments, & Water
  - Plant & Animal tissue
  - Microbial biomass

- **Global Sources of Acidity**
  - Protons from naturally formed carbonic acid
  - Oxidation of biogenic (natural) sulfur gases
  - Volcanic emission of SO_2 that goes to $H_2SO_4^-$
  - Protons from oxidation of NO from lightning
    ($N_2 + O_2 \rightarrow$ Lightning $\rightarrow 2NO \rightarrow H_2O \rightarrow HNO_3^-$)

Anthropogenic

- **Acid Rain**

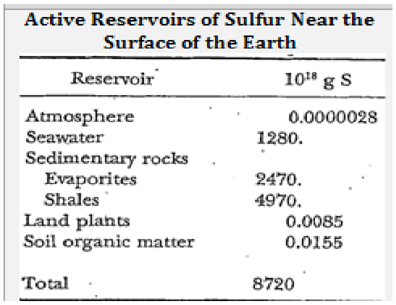
  Adverse Environmental Impacts
  - **Sulfur dioxide** (**SO_2**) emissions can harm plant growth directly
  - SO_2 can oxidize in the atmosphere to **sulfuric acid** (**H_2S0_4**) which falls out as Acid Rain
  - **Acid rain lowers** the **pH** of **poorly buffered lakes**

  Wetlands are **less** Impacted because of the **buffering capacity** of wetland soils, & sulfate & nitrate associated with atmospherically derived sulfuric acid & nitric acid are reduced in most wetland soils & sediments, removing these acids

- **Global Emissions from Industrial Sources (Coal, petroleum refining, etc)**

Sulfur Pools & Fluxes

- **Into the Oceans**
  - rivers are believed to contribute > 200 x 10^{12} grams S/yr to the oceans
  - This is believed to be 2 to 3 times pre-industrial levels.
  - However, compared to the 1.28 x 10^{21} grams S as sulfate already in the oceans, you can't measure the annual increase because the total amount in the oceans is 8 orders of magnitude higher than annual input
- **Into the earth's Near Surface Environment**



Active Reservoirs of Sulfur Near the Surface of the Earth

Reservoir	10^{18} g S
Atmosphere	0.0000028
Seawater	1280.
Sedimentary rocks	
Evaporites	2470.
Shales	4970.
Land plants	0.0085
Soil organic matter	0.0155
Total	8720

Sulfur Reduction

- **Sulfate** **<u>Diffusion</u>**
  - **Sulfate-Sulfur** is the **2nd most abundant anion** in seawater (~885 mg/L)
    └ Chloride is the most abundant (19,000 mg/L), & carbonate/bicarbonate is the 3rd most abundant (28 mg/L)
  - Of course, just as for nitrate, ammonium, oxygen, & soluble reduced iron & manganese, & anything else dissolved, sulfate can diffuse in response to a concentration gradient.
  - In **strongly reducing** <u>coastal sediments & marsh soils</u>, sulfate from seawater **diffuses** in response to a **concentration gradient** from a region of high concentration (seawater) to a region of lower concentration (strongly reduced soils & sediments) where the sulfate disappears.
    └ when this sulfate (SO_4^{2-}) gets into a strongly reducing marsh soil or sediment, it is reduced to sulfide (S^{2-})
    └ a typical reactions is: $\mathbf{SO_4^{2-}} + 4H_2 \rightarrow H_2S + 2H_2O + 2OH^-$
  - Remember that Sulfate is near the bottom of the scale of alternate electron acceptors which means that it requires strongly reducing conditions before it can be used as an alternate electron acceptor in microbial respiration (oxygen, nitrate, manganic manganese, & ferric iron would all be used first)
  - Freshwater marshes & some agricultural soils (for example, flooded rice fields), can & do also contain some sulfide, but the amounts are usually far less than what is encountered in coastal zones.

- **Sulfate Contribution toward Microbial Respiration**
  - The reduction of **Sulfate** (**SO_4^{2-}**) to **Sulfide** (**S^{2-}**) is a **microbial respiration process** in which **SO_4^{2-}** is being used as the **terminal electron acceptor** because all of the more easily used electron acceptors are not available
  - This type of Sulfate Reduction accounted for about **50%** of the **loss of sediment organic matter**
    └ thus for ~ ½ of the organic matter the microbes consumed as an energy source, sulfate was the terminal e- acceptor used

- **Pore Water (A separate finding, supporting something previously indicated for wetland soils)**
  - **pore water dissolved organic matter** (OM) concentration was **higher in anoxic conditions** compared to aerobic
  - this indicates **OM degradation** through **microbial consumption** is **less efficient** under **reducing conditions**

- thus organic matter tends to accumulate in anaerobic conditions such as sediments & reduced porewater

Redox Potential Range for Sulfate Reduction

- **Oxidizing Conditions : in oxidized soils & seawater, <u>inorganic</u> sulfur exists primarily as Sulfate (SO_4^{2})**
- **Reducing Conditions: under <u>strongly reducing</u> conditions, Sulfate (SO_4^{2-}) is reduced to Sulfide (S^{2-})**
  - A typical reaction is: $SO_4^{2-} + 4H_2 \rightarrow H_2S + 2H_2O + 2OH^-$
  - The first product is hydrogen sulfide (H_2S), it is an acid, a highly volatile soluble compound, & toxic to plants
  - In this form (as H_2S), it is toxic to plants (or at least stresses plant growth) at a high enough concentration
    - └ important factor or contributor in the deterioration of marsh plants in some coastal zones
  - Because of the **reactivity** of **S^{2-}** & **H_2S**, & the usual abundance of **reduced**, **ferrous iron** (**Fe^{2+}**) in mineral soils & sediments where sulfide forms, H_2S quickly precipitates with many metals, especially iron, such that most of the sulfide is present as insoluble iron precipitates in most natural soil- & sediment-plant systems
  - Formation of **sulfide** from sulfate is **redox dependent**, occurring in redox potentials between +300 & -200 mv
    - └ Heterogeneous soils & micro-zones of different redox potential may account for some of the discrepancy & the difficulties in making good redox measurements, but it's generally believed strongly reducing conditions are required
    - └ People commonly think of **-150 mv Eh & lower** as necessary for sulfate reduction.
  - The process is also **pH dependent,** occurring mostly between pH **6.8** & **7.0** (overall range of 6.0 – 7.5).
    - └ Compared to the reduction of many other alternate electron acceptors such as nitrate & ferric iron, this is a **very narrow range** for appreciable sulfate reduction.
- **Large Microbial Capacity**
  - There may be a **large microbial capacity** to oxidize hydrogen sulfide in the oxidized zone of sediments, but, this apparently plays a **secondary role** to transformation of **hydrogen sulfide (H_2S)** to **FeS** where **ferrous iron** is present in the <u>strongly reduced zone</u> where hydrogen sulfide is first formed.
  - Reports found bacteria capable of oxidizing sulfide to be abundant with depth in both **aerobic** & **anaerobic** zones
    - └ but until the ferrous iron (Fe^{2+}) was used up in reacting with H_2S, microbial oxidation did not occur
    - └ but since <u>reduced iron oxidizes rapidly</u> in the presence of O_2, you wouldn't expect to find Fe^{2+} where O_2 is present
  - Thus when redox conditions change <u>from oxidized to reduced</u>, the microbes are already present
  - Most of the H_2S added to cores becomes FeS, with small amounts of S^0 & pyrite formed at the deepest depth

- **→ Thus in a system with plenty of reactive iron: reduced sulfur is precipitated as ferrous sulfide with some elemental sulfur & very little hydrogen sulfide forming**

- **Sulfur Oxidation**: occurs when **Sulfides** (**S^{2-}**) are exposed to **oxygen** they will oxidize back to **S^0** & **SO_4^{2-}**

Hydrogen Sulfide (H_2S)

Chemical Characteristics of H_2S

- Colorless Gas, smells like rotten eggs & Odor threshold = 0.05 ppm, 1g dissolves in 242 mL of water at 20˚C (ie. pretty water soluble)

- **Hazard Levels: Safe** (< 0.006 mg/L); **Acute:** toxic to aquatic life at low concentrations**; Chronic: prolonged** > 20 ppm

Water Chemistry

- Sulfide forms insoluble salts with heavy metals & iron that may be present in water, but will settle out for most part, Soluble H_2S will be in equilibrium between undissociated form.
- The secondary S^- is important only at very high pH levels.
- Escape into the atmosphere occurs mostly at low pH, At pH 7 escape is 50% of that in strong acid, & At pH 9, escape is 1% of that in strong acid.

Biodegradation

- **Microbes** in soil & water involved in **oxidation-reduction** reactions that **oxidize H_2S** to **S^0**
  - └ Members of the genera Beggia foal Thioploca, & Thiotrix function in transition zones between aerobic & anaerobic conditions where both molecular oxygen & hydrogen sulfide are found.
  - └ Also, some **photosynthetic bacteria** oxidize hydrogen sulfide to elemental sulfur.
- Members of the families Chlorobiaceae & Chromatiaceae (purple sulfur bacteria) are **obligate aerobes** & are phototropic, & are found in waters with high H_2S concentration.
- The interactions of these organisms form part of the global sulfur cycle

Human Health Effects

- For humans, the problems range from just an odor problem to mild health effects, to definite illness & even death
- Serious health impacts & death are not associated with normal wetlands & natural sediment-water systems, but, are associated with sewer systems, hypolimnetic reservoir waters, sometimes with oil & natural gas deposits & petroleum production.

Symptoms

- Apnea
- fatigue
- insomnia
- coma
- dizziness
- headache
- photophobia
- conjunctivitis
- cornea vesiculation
- lacrimation (excessive fearfulness)
- irritable respiratory system
- gastrointestinal problems

Human Toxicity

- unsatisfactory; 20 pprn = 28 mg/m^3
- symptoms of illness 50 pprn = 70 mg/m^3
- severe toxic effects 200 ppm = 280 mg/m^3 1 min
- man: lethal: 600 ppm/30 min; 800 ppm, immediate (lethality)

Case Studies

Residents of Grand Bois, LA vs. Campbell Wells waste disposal site & Exxon Oil

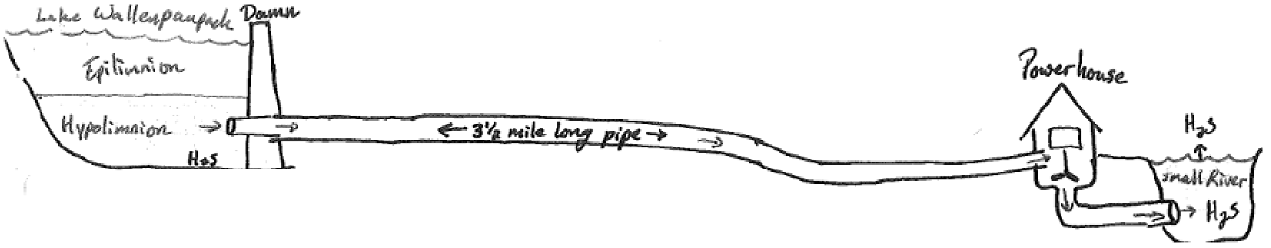
- **Constituents in Oil Waste: likely a fluid mud with petroleum hydrocarbons, barium, sulfate, & common salts**
  - └ It did NOT have **divalent salts** (like Iron) which would precipitate H_2S ($Fe^{2+} + S^{2-} \rightarrow FeS$)
- **Exon claimed the waste was "Biologically Dead"**
  - even though oil field waste is known to be an abundant source of Sulfates & other sulfur compounds, & low levels of divalent metals (which would have allowed insoluble sulfide precipitates to form), thus in the absence of these divalent salts, Hydrogen Sulfide will most likely form – but they never tested for it
  - if they thought the waste was biologically dead, then why did they mix it in the pits?
    - └ Mixing would enhance the oxidation & accelerate microbial degradation of the waste's petroleum hydrocarbons
  - The waste pits had bubbles at the surface
    - └ The bubbles come from microbial respiration of during the reduction of CO_2 to methane
    - └ This proves the waste is biologically ALIVE & that all the sulfate has been used up → H_2S was present

Redox Potential & H_2S in 2 Salt Marsh Sites

Marsh Site	Old Oyster Bayou	Bayou Chitique
Health	Healthy	Un-healthy
Plant Growth	Good	Poor
Elevation	Higher	Lower
Drainage	Moderate – Good	Poor
H_2S Levels	Lower	Higher
Redox Potentials	Higher	Lower
Reduction Strength	Weakly	Strongly

Lake Wallenpaupak & Hydroelectric generating station

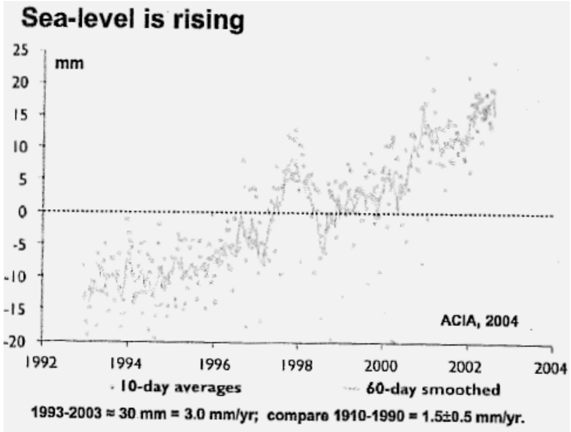
- When the lake stratifies in the late summer the water that is drawn into the 13 mile long pipe going to the hydroelectric plant is cool, strongly reducing, & contains enough H_2S (a few ppm) to cause a bad odor
- They don't use the surface (epilimnion/oxidized) waters b/c the water wouldn't be cool enough for the trout
- They could add other oxidants with > 20% oxygen to oxidize the H_2S; such as: pure Oxygen, hydrogen peroxide (H_2O_2), chlorine (Cl_2), or bleach (NaOCl); but H_2O_2 is too expensive & the others aren't safe
- They could adjust the pH to speed up the oxidation reaction so that HS^- would oxidize slower
- They ended up adding perforated pipes on the bottom of the lake in front of the damn so that air bubbles would purge out the H_2S; despite the risk of harming more people (summer tourism) by releasing the H_2S at the lake instead of the hydroelectric plant, because they found that the smell was less obvious at the lake



Global Warming & Green House Gases (GHG)

Polar Ice Melts

- **Greenland Ice Sheet melt is rapidly accelerating** (23 mi^3 melted in 1996 vs. 53 mi^3 in 2006)
- Part of this increased rate of melting has to do with the **reflectivity & absorbption feed-back loop**
    - 90% of the sunlight that hits the polar ice is **reflected**; whereas, the ocean **absorbes** 90% of the sunlight
      → thus each mile of ice that melts vanishes faster than the mile that melted before it
- 2007 was the first time in known history in which the polar ice had melted enough to allow passage between Russia & Alaska
- By **2060 all of the polar ice will be melted**

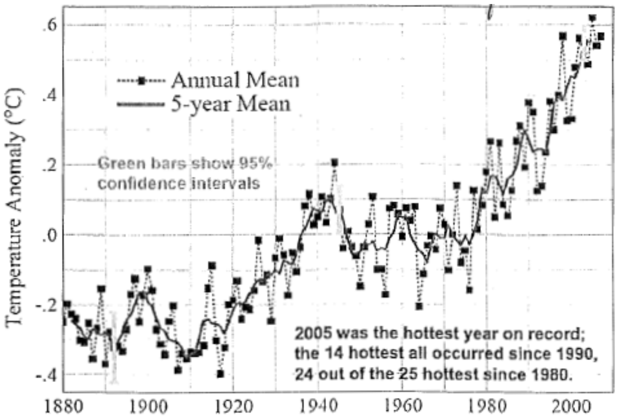


Sea Level Rise

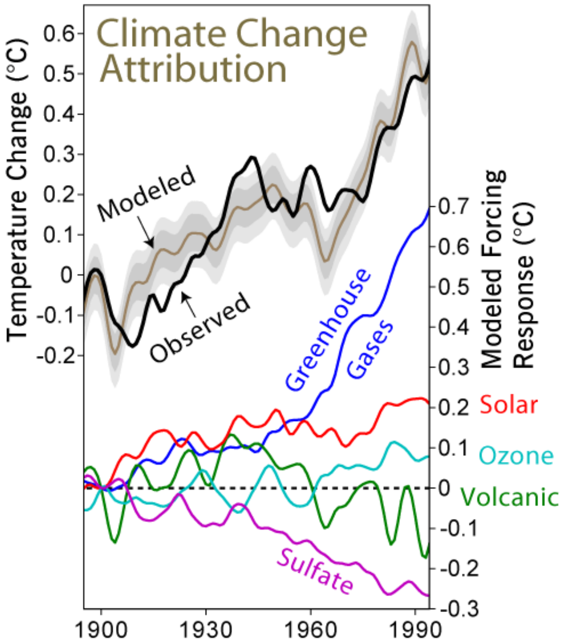
- The last time sea level was higher than it is today was ~130,000 years ago, then it was 20 ft higher
- Sea Level Could rise > 3 feet by **2100** → most of **Louisiana's coastline** will be **underwater**
- by **2500** the Gulf-Coast shore-line will likely run through Baton Rouge

Increasing Air Temperatures

The **Earth is Getting Hotter**

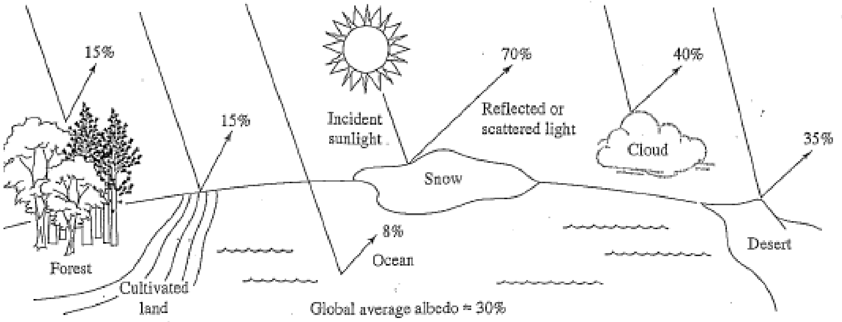


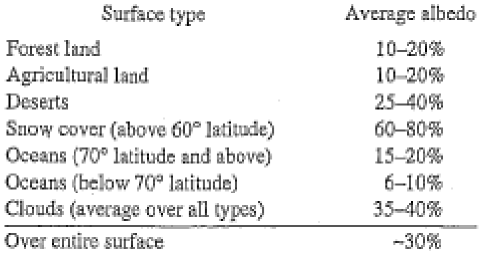
(http://data.giss.nasa.gov/gistemp/graphs)



Heat Balance & Albedo

- There's no net gain or loss of heat at the earth's surface





Surface type	Average albedo
Forest land	10–20%
Agricultural land	10–20%
Deserts	25–40%
Snow cover (above 60° latitude)	60–80%
Oceans (70° latitude and above)	15–20%
Oceans (below 70° latitude)	6–10%
Clouds (average over all types)	35–40%
Over entire surface	~30%

Global Warming & Green House Gases (GHG)

Green House Gases (GHG)

- GHG **absorb** the **heat reflected off earth** instead of letting it escape into space
- GHG allow shortwave radiation from the sun to pass through, but absorb & reflect back the long-wave radiation emitted from the earth's surface, thus trapping it in the atmosphere
- Without the Green House effect, earth would be ~ 60˚F cooler than they are today
- ~50% of the solar energy entering the upper atmosphere is absorbed at the Earth's Surface
- GHG include: **water vapor**, **Carbon dioide** (**CO_2**), **Methane** (**CH_4**), **Nitrous Oxide** (**N_2O**), **Ozone** (**O_3**), **Sulfur hexafluoride** (), **hydroflurocarbons** (), **perfluorocorbons** (), etc.
- GHGs & chlorofluorocarbons gang up to destroy the ozone

There are 3 factors that make a particular GHG important:

1) **amount of gas** in the atmosphere, especially if its concentration is increasing
2) the **relative effectiveness** of a particular gas in **absorbing heat**
3) the **lifetime** of the gas in the atmosphere

- **EU** proposed that **industrialized** countries slash emissions by **25 - 40% below 1990 levels** by **2020**
- **GM** claims they'll cut CO_2 emissions in their North America plants by 40% by 2010 from 2000 levels

Wetlands impact on GHG

- Wetland soils produce & consume GHG → they play an important role in regulating climate change
- Natural wetlands account for **20-25%** of the **global <u>methane</u> emissions**
- They also are an important source of **Nitrous Oxide**, which in turn causes the **depletion of Ozone**
- **CH_4 & N_2O** emissions could be **controlled through the Rice Production Management** of
  - └ Mange the following (1) **Flooding to ↓ redox potentials**, (2) amount of **organic matter**, & (3) amount of **fertilizer** use

Carbon Dioxide (CO_2)

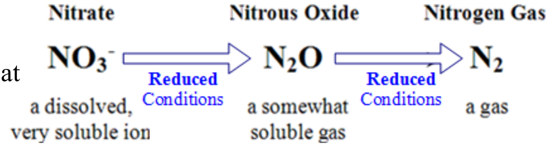
- CO_2 is the worst GHG
- Deforestation contributes 20% of the CO_2 emissions annually on a worldwide basis
- Warmer oceans carry less CO_2 than cooler oceans
  - └ ~50% of the 80ppm glacial-to-interglacial increase can be explained by the change in the solubility of CO_2

Methane (CH_4)

- Methane is the 2nd most important GHG (second to CO_2)
- It has 1/200th the atmospheric concentration of CO_2, but its thermal absorption is more effective
- Methane strongly influences the photochemistry of the atmosphere, accounting for ~15% of the current increase in GHG contribution to global warming
- Methane is an insoluble gas that bubbles to the surface when released to water from strongly reduced sediments
- Under high pressure & very cold conditions in the deed ocean, solid gas hydrates form that trap the methane
  - └ These hydrates are a large potential fuel source (they have 80,000x the amount of natural gas found in conventional reserves)
  - └ Climate change could warm the deep ocean enough to cause these solid hydrates to release the methane ("**methane burp**")
- Total Methane Sources (71% Anthropogenic & 29% Natural Origin) exceed Methane Sinks by 6% → 0.6% ↑
- Rice production is the 4th largest anthropogenic source of methane (b/c its grown in strongly anaerobic flooded fields)

Nitrous Oxide (N_2O)

- N_2O is one of the s**tronger** GHGs in terms of its capacity to absorb heat
  - └ it's a more effective GHG than CO_2 or CH_4
  - └ contributes 4% to the total GHG effect in global warming



- Agriculture causes 50-70% of the anthropogenic emissions of CH_4 & N_2O (Rice production generates a lot of N_2O)

Sulfates

- Non-absorbing sulfates directly reflect radiation & increase reflection by clouds → cooling effect
- Sulfates emitted from jet engine exhaust can counteract the warming effect of typical GHGs

Global Warming & Green House Gases (GHG)

Carbon Sequestration

- **Removing Carbon** from the cycle where **organic carbon** is either **combusted as fuels** or **oxidized by microbial activity** (in soils, plants, & sediment-water systems) **rapidly cycles back** to **CO_2**
- There seems to be a **strong correlation** between **changes** in **temperature** & 2 GHG (**CO_2** & **Methane**) going back **150,000** years before present
    - Usually when one goes up, so will the other 2
    - However, in some cases the temperature seems to go up before CO_2
    - This just shows how complex climatic processes are & how they can't be explained any one factor alone
- **Iron fertilization hypothesis**
    - Dump iron into the oceans b/c it's the most limiting nutrient to primary production → it would ↑ algal growth → ↑ CO_2 intake
- By ↑ **soil organic Carbon content** by just 0.01% per yr. we could stop the ↑ in Carbon in the atmosphere
- Trap industrial emitted CO_2 & inject it deep in the earth

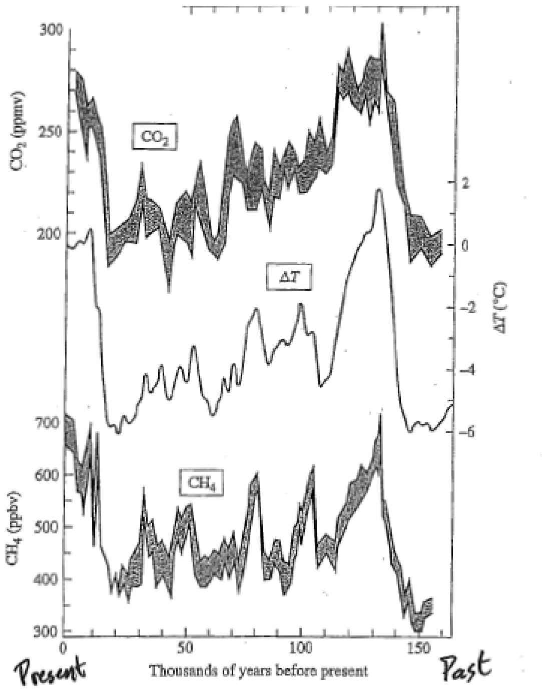
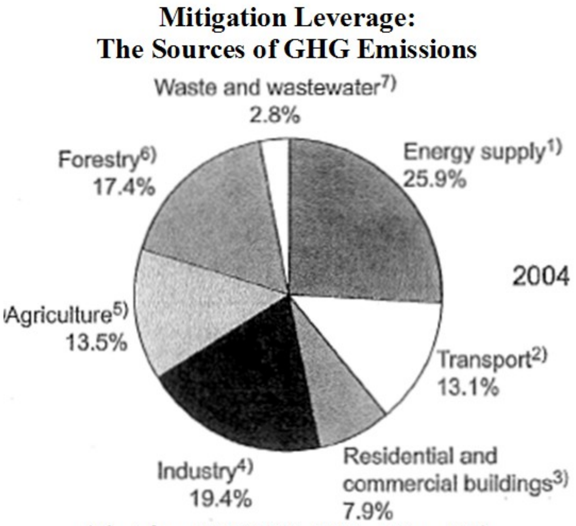
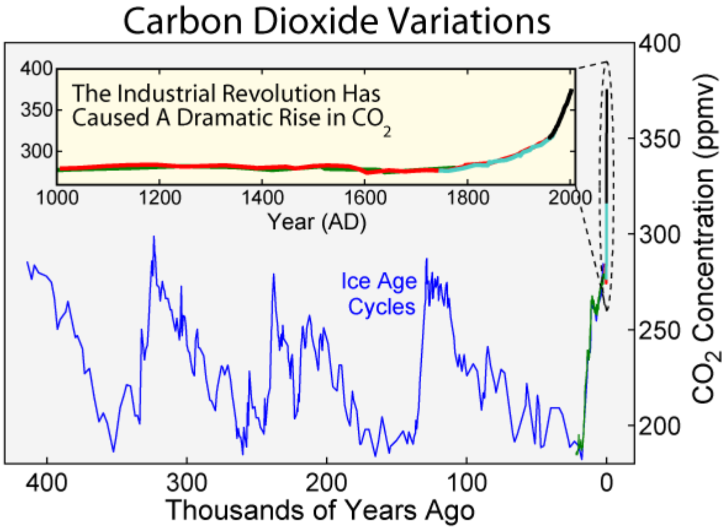
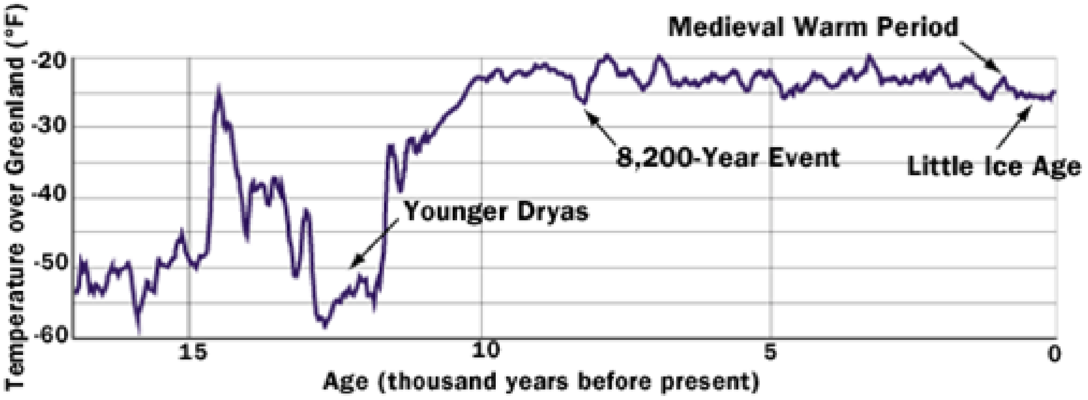


Figure 6.21 Antarctic ice-core records of local atmospheric temperature, and corresponding air concentrations of carbon dioxide and methane for the past 160,000 years. *Source:* J. T. Houghton et al., eds. (1990). *Climate Change: The IPCC Scientific Assessment* (Cambridge, U.K.: Cambridge University Press).



(Chart from IPCC 2007: WG3, AR4, p. 105)





Trace & Toxic Metals

Definitions

Types of Metals

- **Heavy** metals: metals that can be or are **toxic** (**Copper, Lead**, **Zinc**)
- **Trace** metals: metals that are **essential** for **plant & animal nutrition**, these can be toxic under some conditions (**Copper**, **Iron**, **Manganese**, **Zinc**)
- **Toxic** metals: Metals that are **not essential** for plant & animal nutrition (**Aluminum, Cadmium, Lead, Mercury)**
- **Non-metals** that get lumped in with Heavy Metals: **elements like Arsenic** (As), **selenium** (Se), etc.

Availability

- **Chemical** availability: **how available metals** are to **aqueous or various chemical extractions**
  - **Soluble metals** are certainly **chemically available**
  - Used as a **quick prediction** of what the **toxicity** might be to the surrounding environment (exchangeable metal extractions)
- **Biological** availability: **how readily metals are taken up by plats, land animals, & aqueous species**
  - this is what chemical availability is trying to quickly approximate

Target Species : **organisms** that may be **affected** by **trace** or **toxic metals**

pH : a measure of how acidic or basic a system is, **lower pHs levels favor the release of metals to soluble & available forms**

Redox Potentials : a measure of the **intensity of oxidation** & especially **reduction** of a soil or sediment-water system

- **pH** & **Redox potentials** have a **very strong affect** on the **mobility** (ability to go into solution) & the **biological availability** of metals

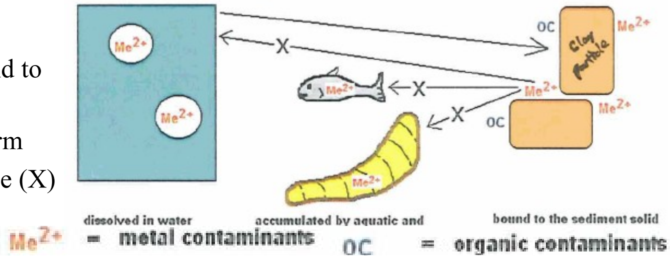
Importance

Interest in Metals

- Many metals are essential for nutrition & must be available in adequate amounts; while others are just toxic
- Trace & toxic metals can be toxic to plants, wildlife, & humans under some conditions
- Metal-contaminated wastes often require special disposal/treatment, as they pose an ecosystem toxicity/health threats
- **Biochemistry of Metals**
  - **Concentrations** of metals can be **important** to the **magnitude of problems** with trace & toxic metals
  - the **mobility** & **biological availability** of metals is often **more important**, because they can be independent of concentration

Contaminants in Sediment-Water Systems

- There's a strong tendency for metal contaminants to be bound to clay particles (ie. sediment-solid particles)
- this is good because it locks the toxins up & ↓ the risk of harm
- We don't want these metals to be released into aqueous phase (X)



Sources of Trace & Toxic Metals

Primary Sources: all metals occur naturally in all soils

Secondary Sources: **industrial discharges**, **ore deposits** & **mining activities**, **sludge disposal**, **land fills**, **combustion of some fuels** & **waste incineration** releases to the atmosphere (mercury is especially volatile)

Background (uncontaminated) Levels

- Trace & toxic metals are found in all soils & sediments, & in non-contaminated substrates their levels are usually low
- **Soil Texture** (sand, silt, & clay ratio) determines to a large extent the background elemental concentrations
  - └ clays will have the most trace & toxic metals because their ionic conditions cause the metals to be strongly bound to them
  - └ sands will have the least metals (even if exposed to the same amounts) because they aren't able to hold onto them

Uncontaminated Soils

Metals	Levels (ppm)
Mercury (Hg)	0.03
Cadmium Cd)	0.06
Arsenic (As)	5
Lead (Pb)	10
Copper (Cu)	30
Nickel (Ni)	40
Zinc (Zn)	50
Chromium (Cr)	100
Phosphorous (P)	600
Manganese (Mn)	600
Magnesium (Mg)	5,000
Calcium (Ca)	13,700
Carbon (C)	20,000
Iron (Pb)	38,000
Aluminum (Al)	71,000

(Note: 1% = 10,000 ppm)

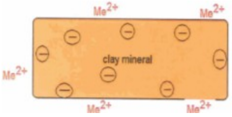
Trace & Toxic Metals

General Chemical Forms

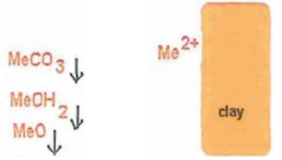
- We're interested in the conditions in which metals go from Potentially to Readily Available

Readily Available

- **Dissolved** (**Water soluble** metals)
- **Exchangeable**
  - Weak adsorption to clay surfaces



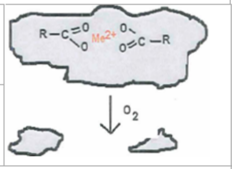
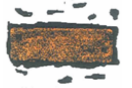
Soil & Sediment pH Effect on Metal Precipitation & Adsorption

Low pH (acid)	Near Neutral to Alkaline pH
 **More Metals in Solution**	 **Precipitation** **Adsorption**
Under these conditions metals are **<u>Readily</u> Available**	Under these conditions metals are **<u>Potentially</u> Available**

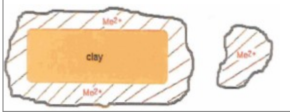
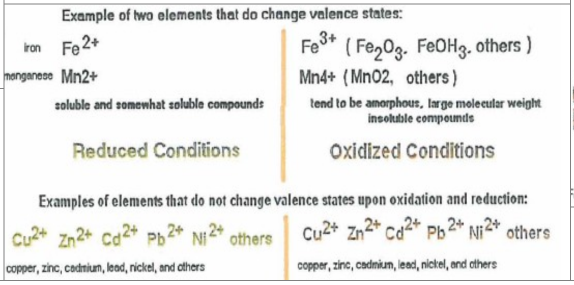
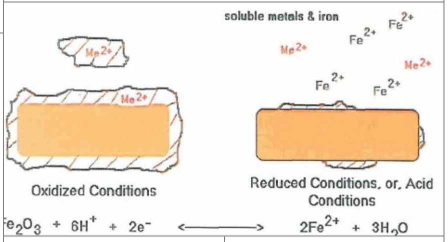
Potentially Available

(most metals in both contaminated & un-contaminated Soils are found here)

- Exchangeable
- **Precipitated** Oxides, hydroxides, carbonates, etc.
- **Bound to insoluble humic materials** (organic matter)
  - Organic matter + O_2 → less Organic Matter + CO_2

Metals bound to Organic Matter	**Long-term Response** of **Wetland OM** to an ↑ **in Oxidation** Conditions	**Role of OM** Content in **Affecting** the **Metal Retention** Capacity of Soils
 OM	**Reduced** **Oxidized** 	**<u>Low</u> OM content**  **<u>Lower</u> metal retention capacity** **<u>High</u> OM content**  **<u>Higher</u> metal retention capacity**
This is usually a **strong attraction**	As we go **from Reduced** to **Oxidizing** conditions, **metals** tend to be **removed from the OM**	OM particulates & Coating on Clay mineral particles

- **Bound to amorphous oxyhydroxide precipitates** of iron & manganese

Metals Bound by Iron Oxides are **<u>trapped</u>** under **Oxidizing** Conditions	**Changes** in **Redox Potentials & pH** affect the **solubility & Biologic Availability** of many trace & toxic metals For some, it's a matter of **changes in valence state**, while others don't change their chemical valence state	**Metals Bound by Iron Oxides can be <u>released</u> under Reducing Conditions**
		
As long as **conditions remain oxidizing** the **metals will be trapped** (because of their strong, tight bond to the clay particle)		Mixture of **<u>insoluble</u> ion compounds** **Soluble & Semi-Soluble** ion compounds

Example of two elements that do change valence states:

	Reduced Conditions	Oxidized Conditions
iron	Fe^{2+}	Fe^{3+} (Fe_2O_3, $FeOH_3$, others)
manganese	Mn2+	Mn4+ (MnO2, others)
	soluble and somewhat soluble compounds	tend to be amorphous, large molecular weight insoluble compounds

Examples of elements that do not change valence states upon oxidation and reduction:

Reduced Conditions	Oxidized Conditions
Cu^{2+} Zn^{2+} Cd^{2+} Pb^{2+} Ni^{2+} others	Cu^{2+} Zn^{2+} Cd^{2+} Pb^{2+} Ni^{2+} others
copper, zinc, cadmium, lead, nickel, and others	copper, zinc, cadmium, lead, nickel, and others

$$Fe_2O_3 + 6H^+ + 2e^- \longleftrightarrow 2Fe^{2+} + 3H_2O$$

- **Precipitated** as **insoluble sulfides**
  - **Metal sulfides** are **very insoluble** & **stable** as long a **Redox Conditions** remain **Strongly Reducing**

Metals Bound as <u>Insoluble</u> Metal Sulfide Precipitates	
Reduced Conditions	**Oxidized** Conditions
Insoluble Metal Sulfide Precipitate	**Metals are Released as Sulfide is Oxidized to Sulfate**

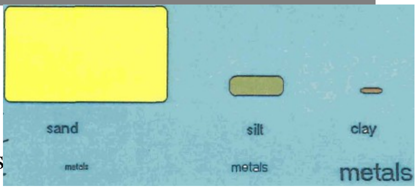
$$MeS\downarrow \xrightarrow{oxygen} Me^{2+} + SO_4^{2-}$$

Unavailable

- Bound within the crystalline lattice structure of clay minerals
- Unavailable except for the extremely slow geological weathering (decomposition) of clay minerals

	Availability	Toxicity Risk	Solubility	Attraction Strength	pH	Potentially Available	Metals are Bound by	Redox Conditions Reducing	Oxidizing
☹	**Readily** Available	**Very High**	Soluble	Weak adsorption	Low pH (acidic)		Humic Material	Metals **bound** to OM **High** OM Content **Higher** metal **retention**	Metals **Removed** from OM **Low** OM Content **Lower** metal **retention**
😐	**Potentially** Available	**Moderate**	Exchangeable to Insoluble	Precipitated to Strongly Bound	Neutral to Alkaline		Iron Oxides	Metals are **Released** **Soluble & Semi-soluble** **Acidic (low pH)**	Metals are **Trapped** **Insoluble**
☺	**Unavailable**	**Very Low**	Insoluble	Strongly Bound (crystalline lattice structure)	High pH (basic)		Sulfides	Metals are **Bound** **Insoluble Sulfide precip.** **Stable**	Metals are **Released** **Soluble Sulfate** **Unstable**

Soil Particle Size & Contaminant Retention



- Metal Retention ↑ with ↓ soil particle size
- Inverse relationship between soil particle size & particle's ability to retain metals
- Small particles have higher bidning strength (attractive forces) than larger particles

Major Disposal Options for Contaminated Dredged Sediments

Sub Aqueous (underwater) Disposal

- Disposal does not conflict with important economic or ecological productivity
- Application to especially productive aquatic ecosystems

👍 **Confined**:

i. **Mounded**: isolated as a **stable mound** (**low energy** water column) with **cap of clean material**
ii. **Confined** in a **depression** &/or **capped with clean material**

👎 **Unconfined**: wide dispersal with currents if in shallow water

Intertidal Disposal

👍 **Habitat Development Confined by boundary structure (resistant to erosion) & capped with clean sediments**

👎 **Unconfined habitat development → some erosion & some consolidation**

- **Non-biological purpose** : Shoreline stabilization / modification, or Confined by boundary structure

Upland Disposal

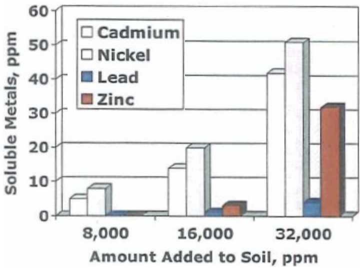
👍 **Long-Term confinement** for under ponded (**flooded**) conditions, for disposal purposes only

- **Interim confinement** for contaminated sediments for dewatering, consolidation, & possibly treatment prior to transport & reuse for productive purposes
- **Unconfined upland** – not specifically intended for habitat development, but is subject to biotic colonization with time
- **Use for fill & other construction/engineering purposes**

👎 **Habitat development** – application for specific biological purpose

👎 **Agricultural soil amendment & land reclamation**

Metal Retention Capacities



Capacity for soils to retain metals depends greatly on soil properties

- **Best retention** occurs where there is High Clay & **High Organic Matter Content**
- **Lead** tends to be the **least soluble** because the soils & sediments **hold on to it more**

Case Studies

Air Force Bases

- Site 1: **high clay content**, **pH > 7** (likely because of calcium carbonate in the soils) → **Excellent** Containment
- Site 2: **Sandy Soils, lower pH, oily organic liquid** with elevated levels of contaminants → **Very Poor** Containment

Battery Recycling Plant

- Batteries are thrown into a pile outside (→ cracked & weathered)
- trees around a nearby swamp began to die off, when swamp water was tested the metal on the tester bubbled
- Battery (sulfuric) Acid was in high concentrations in the swamp, facilitated by the sandy soil & high rainfall

Aluminum Refinery Plant

- Extracts Aluminum from African Boxite Ore using extremely high temperatures & sodium hydroxide to get high pHs
- **Red Mud** byproduct was initially dumped in the Mississippi river, then dumped in artificial Ponds until they filled up
- Even though they neutralize the pH of the mud before dumping it in the ponds, they still couldn't get plants to grow
- mixing the mud with marsh soil or compost material →contaminants become locked away & plant growth is favored

Nitrogen (N) Chemistry

❖ **Importance** of Nitrogen

- one of the **most limiting nutrients** **regulating the productivity** in terrestrial, wetland, & aquatic **ecosystems**
- N is the **most abundant** **gas in the atmosphere**
- N reactions within the biosphere are the **key regulators of ecosystem productivity & functions**
- **Anthropogenic production of Nutrient N** has **greatly** ↑ **amount of N in the environment**

❖ **Forms** of Nitrogen

➢ **Inorganic** Nitrogen

- present only in **Dissolved** forms

Dinitrogen (N_2)

- the **most common form** of Nitrogen, making up **~78% of the atmosphere**
- colorless at room temperature, slightly soluble in water, & **very stable**, the N in N_2 is **triple bonded** (**N≡N**) → **fairly inert**
- **High activation energy** is needed to **break the bond** → ↑ demand for other forms of N since most organisms can't directly use N_2
  - └ Biologically this triple bond is broken by organisms capable of fixing N_2
  - └ **Industrial fixation** of N_2 is done via the **Haber-Bosch process** (**forming of N fertilizers**) → this alters the global N balance
- Dinitrogen is limiting in most ecosystems, but the Anthropogenic production of Nutrient N has greatly ↑ amount of N on earth

Ammonia (NH_3) / Ammonium (NH_4) Nitrogen

- **Ammonia** (NH_3) : $CH_4 + N_2 \rightarrow NH_3$ or $3H_2 + N_2 \rightarrow NH_3$ **(higher pH)**
  - colorless & **readily soluble in water**; ionic form is present under **acidic** conditions (unionized under basic conditions)
    - └ Used in fertilizers as anhydrous ammonia injected directly into the soil
- **Ammonium** (NH_4^+) : $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$ **(lower pH)**
  - Used in **fertilizers** as **NH_4 salts** (NH_4 nitrate or NH_4 sulfate) & applied to **upland** or **aerobic soils** is **rapidly** **oxidized** to **Nitrate**
    - └ Intensive fertilizer use & excessive rainfall or irrigation → **excessive levels of Nitrate (NO_3^-) in ground waters**

Nitr<u>i</u>te (NO_2^-)

- Readily Soluble in water & **highly mobile in** soils
- it's a relatively **short-lived** form of N

Aerobic Conditions: **Nitrite (NO_2^-)** $\xrightarrow{\text{Oxidized}}$ **Nitrate (NO_3^-)**

Anaerobic Conditions: **Nitrite (NO_2^-)** $\xrightarrow{\text{Reduced}}$ **Nitrous Oxide (N_2O)**

Nitr<u>a</u>te (NO_3^-)

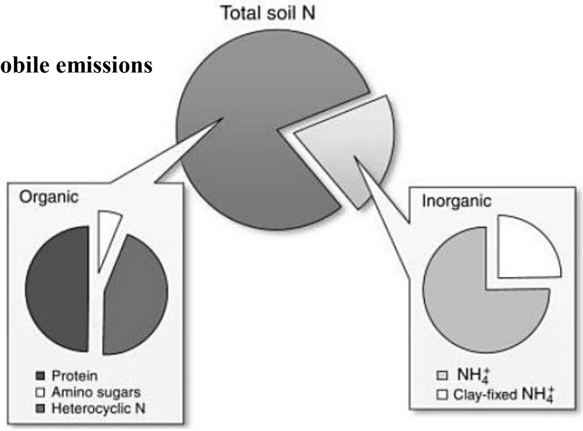
- Readily Soluble in water & **highly mobile in** soils, its formed during the Nitrification of Ammonia N
- It is used with Ammonium (NH_4^+) by plants & microbes as the nutrient forms of Nitrogen, & an electron acceptor by microbes

Nitrous Oxide (N_2O) "laughing gas"

- Colorless gas, **slightly soluble in water**, its an **intermediate** in the N cycle, it is an **end product of Dinitrification**

Nitric Oxide (NO)

- Not a major form in the N cycle, its produced by **industrial & automobile emissions**



➢ **Organic** Nitrogen

- present in both **Dissolved** & **Particulate** forms
- important to life but not so important to wetlands biogeochemistry

Proteins "**building blocks of life**"

- **polymers of amino acids**, accounts for **~50%** of the organic N

Nucleic Acids

- **polymers of mononucleotides**, accounts for **< 1%** of total soil N

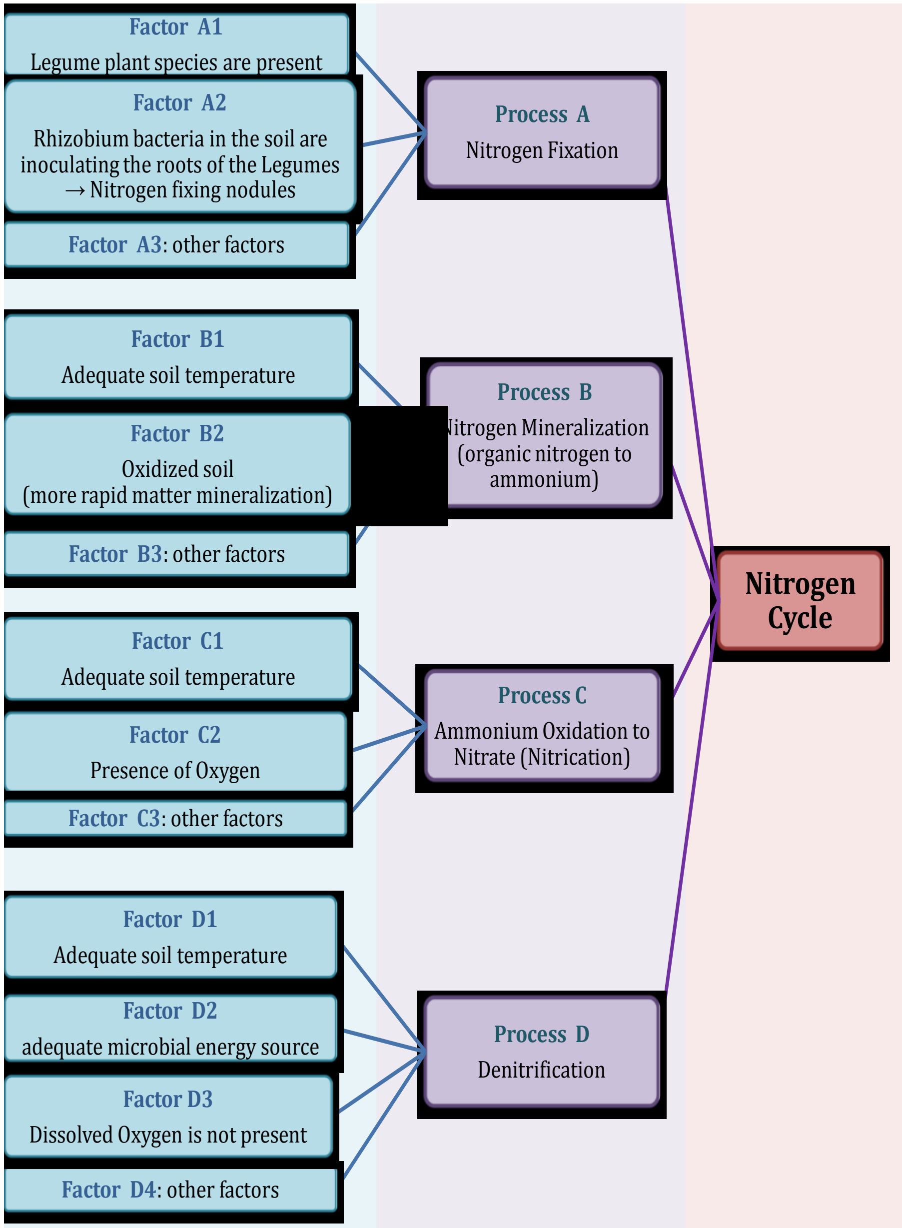
Amino Sugars :

- **Structural components** of a broad group of substances (such as **Mucopolysaccharides** & **Chitin**)
- These Amino Sugars or **Nitrogen-containing carbohydrates** = **5 – 10 %** of the Organic N in the **surface layer of most soils**

Urea

- **Waste produce of animals & humans,** it can also be produced industrially, commonly used as **fertilizers**

❖ The Nitrogen Cycle



Factor A1
Legume plant species are present

Factor A2
Rhizobium bacteria in the soil are inoculating the roots of the Legumes → Nitrogen fixing nodules

Factor A3: other factors

Process A
Nitrogen Fixation

Factor B1
Adequate soil temperature

Factor B2
Oxidized soil
(more rapid matter mineralization)

Factor B3: other factors

Process B
Nitrogen Mineralization
(organic nitrogen to ammonium)

Factor C1
Adequate soil temperature

Factor C2
Presence of Oxygen

Factor C3: other factors

Process C
Ammonium Oxidation to Nitrate (Nitrication)

Factor D1
Adequate soil temperature

Factor D2
adequate microbial energy source

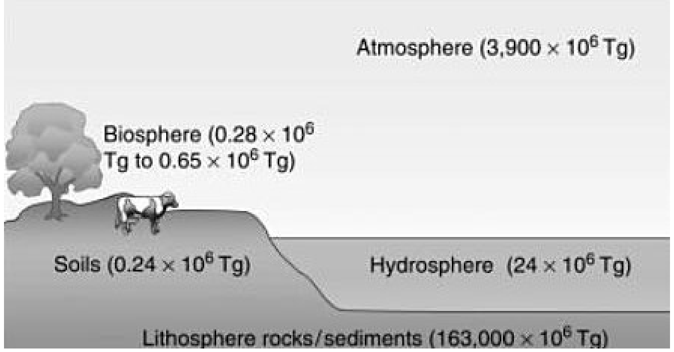
Factor D3
Dissolved Oxygen is not present

Factor D4: other factors

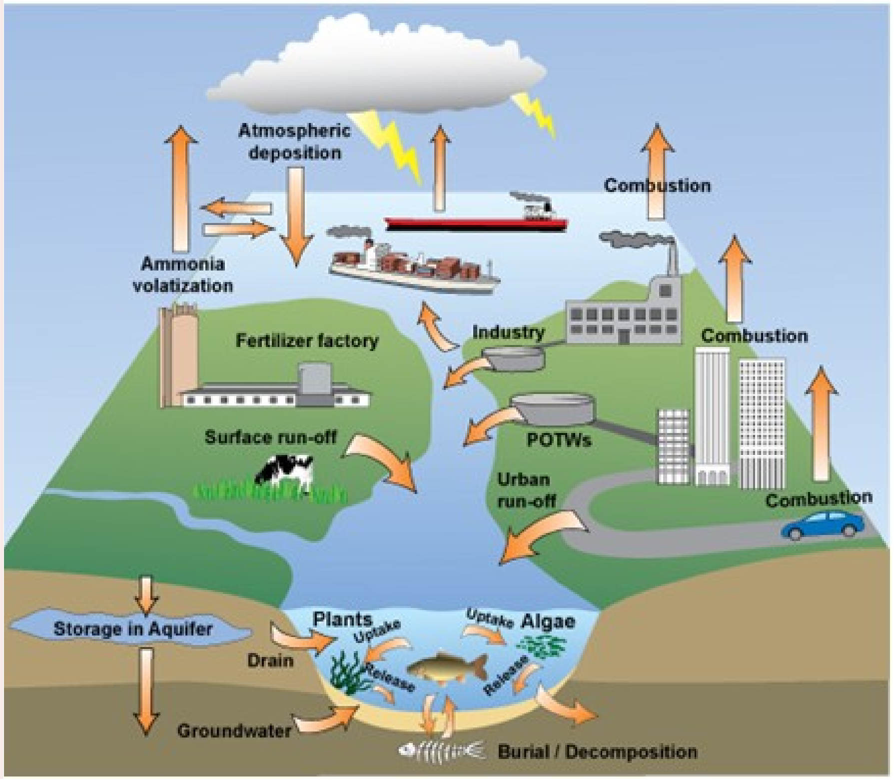
Process D
Denitrification

Nitrogen Cycle

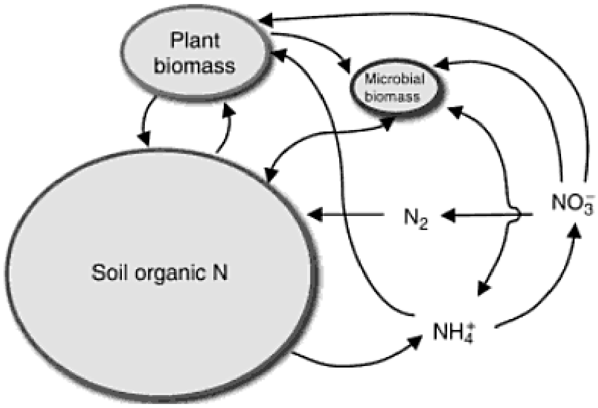
General Reservoirs of Nitrogen

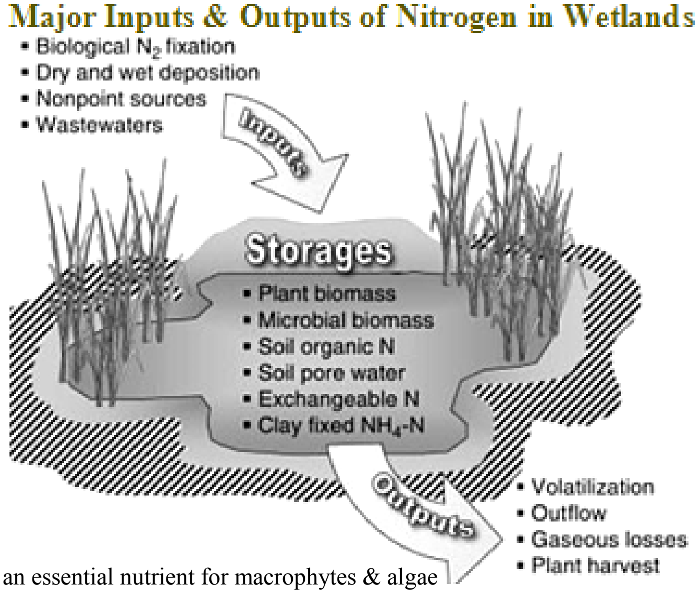


General Nitrogen Cycle



➢ Nitrogen Cycles in Wetland Ecosystems

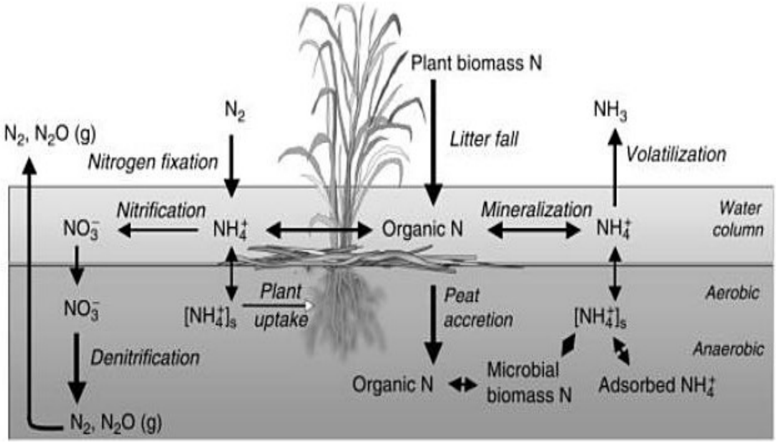


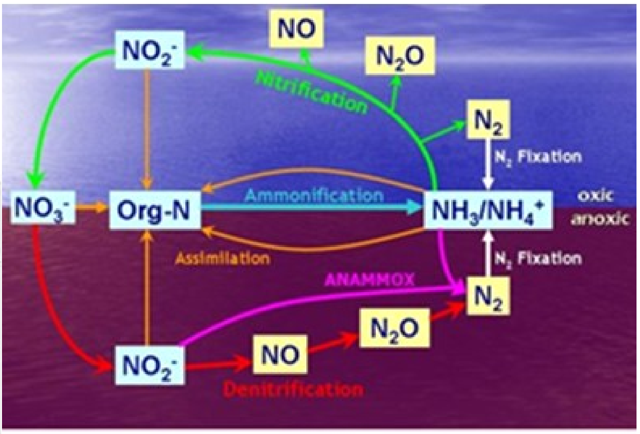


○ Reservoirs of N in Wetlands

- **Plant Biomass** N
  - **Legumes** (clover, alfalfa, peas, beans, peanuts, etc.)
  - N is the 2nd largest component of the plant biomass & it is an essential nutrient for macrophytes & algae
- **Particulate Organic** N
  - **largest storage** of N is present in **soil organic matter**
  - its comprised primarily of **humus & complex proteins → Not readily bioavailable**
    - └ even though Soil Organic N has the largest pool size, it is still considered **limiting**, because it is so **difficult to mineralize**
- **Microbial Biomass** N
  - Only represents 0.5 – 3.0 % of total N, but is a **key component to the N cycle**
    - └ Microbes do a significant amount of the work in the system by utilizing organic & inorganic forms of N for cell growth
  - This is the most active N pool, & regulates the amount of bioavailable N
  - These microbes use detrital organic matter (from dead plants) as an energy source to breakdown organic N into ammonium N
- **Dissolved Organic** N **(DON)**
  - DON = < 1% of total soil Organic matter
  - It can be important in oligotrophic wetlands where most of the N is in dissolved organic form (its extracted from pore waters)
- **Inorganic Forms** of N
  - Important because the N cycle works through the transformation of these typically unstable inorganic forms (NH_4^-, NO_2^-, NO_3^-)
- **Gaseous End Products**
  - Gaseous forms of N include **NH_3^-, N_2O, & N_2**, which are readily lost to the atmosphere, & = **< 1%** of the total N in wetlands
  - N is exported from wetlands through **Ammonia volatilization** under **alkaline** conditions where **unionized** Ammonia is transported from soils & water column to the atmosphere in its gaseous form.

Nitrogen Transformations in Wetlands





➢ Nitrogen Transformation Processes

1) Fixation: Atmospheric non-nutrient N_2 → Nutrient (Organic) N

1a) Fixation of **Atmospheric N_2 Precipitation**

1b) Chemical Fixation of **N_2** (fertilizer production)

1c) **Biological** fixation of **N_2** to nutrient form

- Can occur in **Aerobic** & **Anaerobic** soils & sediments, but N-fixation organisms work best in oxygen deficient environments
- Processes in the root nodules of Legumes tend to **reduce** oxygen content in the nodules in order to ↑ efficiency of N fixation
- ★ N fixation can occur in **Anaerobic** environments because the **oxygen limitation** is **localized to the root nodule**

2) Mineralization

└ the **conversion** of **Nutrient N** from its **Organic to Inorganic Forms**

2a) Ammonification: Organic N → NH_3^+ → NH_4^+

└ **Biologic transformation** of **Organic N** to **Ammonium** (**NH_4^+**)

- process is strongly related to **organic C** decomposition, b/c a large amount of N in soil OM & plant detritus is bonded to C
- in **Aerobic** & **Anaerobic** conditions, but is **more rapid** under **Aerobic** conditions

2b) Nitrification: NH_4^+ → NO_2^- → NO_3^-

└ **Biological Oxidation** of **Ammonium** to **Nitrate** under **Aerobic** conditions **only**

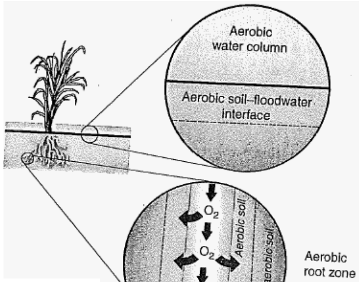
- **Chemoautotrophic** bacteria

Nitrosomonas sp. **Oxidizes Ammonium** to **Nitrite**

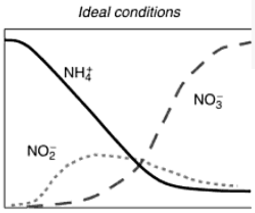
$$\mathbf{NH_4^+} + 2H_2O = NO_2^- + 6e^- + 8H^+$$
$$1.5O_2 + 6e^- + 6H^+ = 3H_2O$$
$$NH_4^+ + 1.5O_2 = \mathbf{NO_2^-} + H_2O + 2H^+ \qquad G° = -272\ kJ/mol$$

Nitrobacter sp. **Oxidizes Nitrite** to **Nitrate**

$$\mathbf{2NO_2^-} + 2H_2O = 2NO_3^- + 4e^- + 4H^+$$
$$O_2 + 4e^- + 4H^+ = 2H_2O$$
$$2NO_2^- + O_2 = \mathbf{2NO_3^-} \qquad G° = -75\ kJ/mol$$



- **Methane-oxidizing** bacteria
  - Obligate aerobes that oxidize ammonia at **slower rates** than the chemoautotrophs
- **Heterotrophic** bacteria & **fungi**
  - Heterotrophic nitrifiers that use organic substrates as the energy source & **gain no energy** from the oxidation of **ammonium**



3) Assimilation:

└ Assimilation (uptake by plants)

- can occur in **Aerobic** & **Anaerobic** soils & sediments

4) Immobilization: NO_3^- → Organic N

└ Conversion of **inorganic N** to **organic forms** such that Ammonium (**NH_4^+**) is assimilated into the biomass of plants & microbes

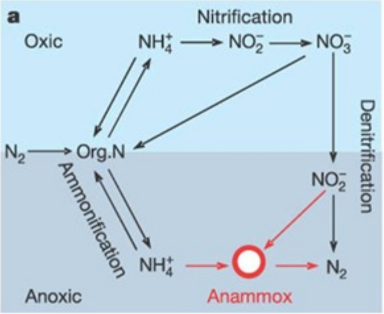
- can occur in **Aerobic** & **Anaerobic** soils & sediments, but is slower in Anaerobic conditions

5) Denitrification: NO_3^- → NO_2^- → N_2 or N_2O

└ **Electrons** are **added** to **Nitrate/Nitrite** via **Microbial Respiration** causing the **reduction** of N to **Nitrous Oxide** or **Nitrogen gas**

- It's a **Biological** process nearly 50% of all anaerobic & facultative anaerobes can perform in **Anaerobic** soils & sediments
- Nitrate is used as the alternate electron acceptor since oxygen is limiting

○ Other More Recently Discovered Processes

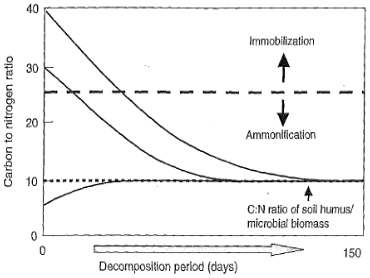


- **Anaerobic Ammonium Oxidation (ANAMMOX)**
  - **Ammonium oxidation** to **dinitrogen** using **Nitrite** as an **electron acceptor**
  - occurs only in **Anaerobic** conditions
  - Accounts for 67% of the N_2 formed in continental shelf sediments (vs. 33% was from Dinitrification)
- **Dissimilatory Nitrate Reduction to Ammonia (DNRA)**
  - Under **highly reducing** conditions, obligate **Anaerobes** cause **Nitrate** to be **Reduced** to **Ammonium** instead of Nitrogen gas
- **Nitrifier Denitrification** (occurs only in **Aerobic** conditions)
- **Aerobic Denitrification** (occurs only in **Aerobic** conditions)

❖ Nitrogen Transformation Processes in more detail

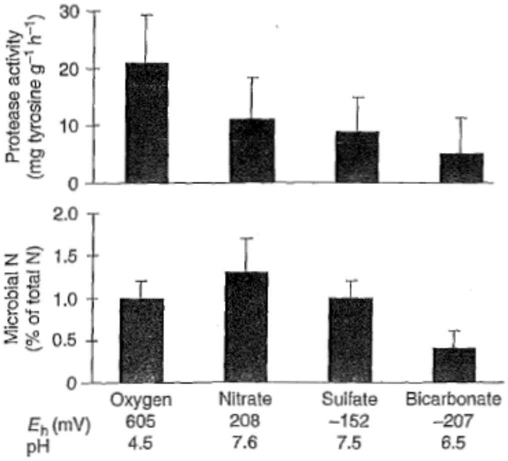
➢ Mineralization of Organic N

- **C:N Ratio Concept: Decomposition** of **Organic Matter** & **Detrital C:N ratio**
  - **Differences** in the **microbial nitrogen requirements** explains why **ammonium release** is **higher under anaerobic** conditions
  - **Organic substrates** with **wider C:N ratios stimulate immobilization**, whereas those with **narrower ratios** favor **ammonification**
    - Carbon assimilation by **aerobic** microbes is ~20 – 60% (note: the fungi are more efficient than the bacteria)
    - Carbon assimilation by **Anaerobic** bacteria is only 5-10%
    - If the C:N ratio is **> 25**, than **net <u>immobilization</u> of inorganic N** will occur
    - If the C:N ratio is < 25, than net **<u>ammonification</u> will cause the release of inorganic N** (b/c microbial demand of N has been met)
    - Under **Anaerobic** conditions, if C:N ratio **> 100**, then **buildup of organic matter** occurs (b/c low microbial demand for N)
    - Under **Anaerobic** conditions, if C:N ratio **<100**, then **ammonium will be released** (b/c microbes are decomposing the detritus)

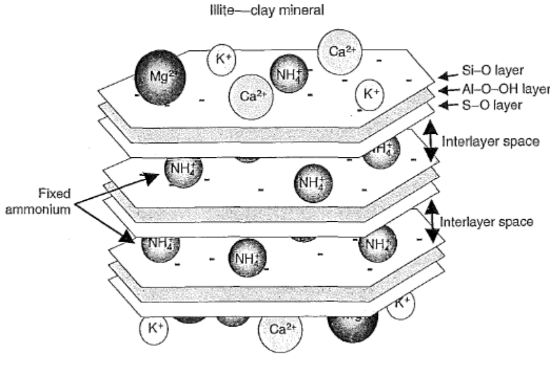


○ Microbial Degradation of Organic N

Soil **Redox Potential**
influences **Mineralization of Organic N**



○ Ammonia Fixation



Ammonium fixation in clay lattice

○ Regulators of Organic N Mineralization

- **Substrate quality**
- **Carbon to Nitrogen Ratio**
- **Microbial biomass & enzyme activity**
  Mineralization of Organic N is directly proportional to the amount of microbial biomass & enzyme activity
- **Temperature**
  The **rate of ammonification** ↑ with an ↑in soil **temperature**
- **Redox Potential & Hydrology**
  Redox status (regulated by the water table & loading of alternate e^- acceptors) have substantial control over organic N mineralization.
- **Soil pH**
  In most wetlands, pH is buffered ~7
  in **well drained** soils, **soil pH** ↓ as **[nitrate]** ↑ during **mineralization**
  The **optimum pH range** for **ammonification** is **6.5 – 8.5**

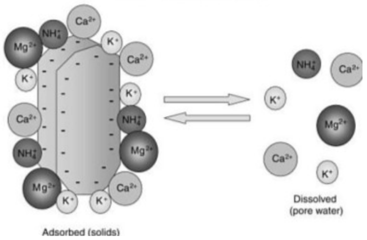
TABLE 8.3
Mean Organic N Mineralization Rates (mg N kg^{-1} day^{-1}) for Detritus and Soil from Northern Everglades Wetlands Soils (One Standard Error in Parentheses) ($n = 8$)

Redox Status	Detritus	Soil (0–10 cm)	Soil (10–30 cm)
Oxygen (aerobic)	237 (26.1)	143 (8.4)	74.9 (5.6)
Nitrate reducing	59.5 (12.0)	17.1 (6.3)	3.95 (1.1)
Sulfate reducing	36.0 (7.9)	8.94 (3.7)	3.05 (1.5)
Methanogenic	19.3 (2.0)	4.54 (1.3)	1.24 (0.2)

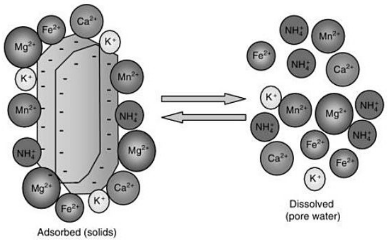
○ Ammonia Adsorption-Desorption

Partitioning of Ammonium between soil cation exchange complexes & pore water

<u>Aerobic</u> Ammonium Adsorption



<u>Anaerobic</u> Ammonium Adsorption



➢ Ammonia Volatilization

- **Ammonia (NH_3) Volatilization** is **low** at **pH < 7.5**, & ↑ **rapidly** as pH ↑ above **7.5**

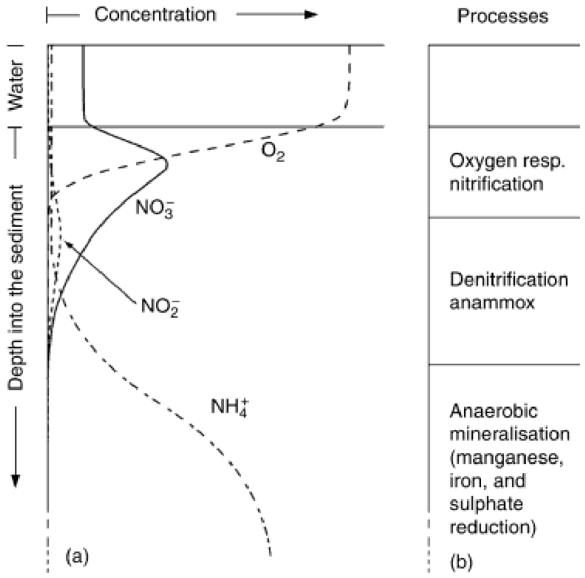
➢ Nitrification

- **Regulators of Ammonium Oxidation :** 1) **[Ammonium]**, 2) **O_2 Availability**, 3) **pH, Alkalinity, & CO_2**, 4) **Temperature**, 5) **Nitrifying Population**, 6) **Cation exchange capacity**, 7) **Redox Potential**

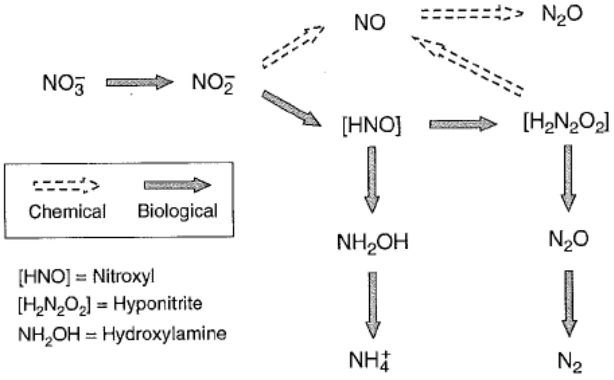
➢ Anaerobic Ammonium Oxidation

$$5NH_4^+ + 3NO_3^- = 4N_2 + 9H_2O + 2H^+$$

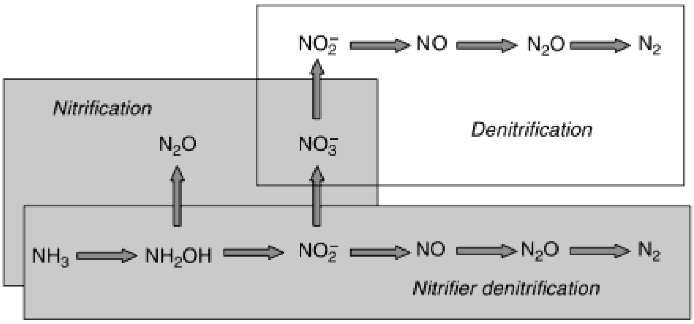
$$NH_4^+ + NO_2^- = N_2 + 2H_2O$$



➢ Nitrate Reduction



Pathways and intermediate products during nitrate reduction reaction.



Schematic of pathways showing denitrification during nitrification reaction