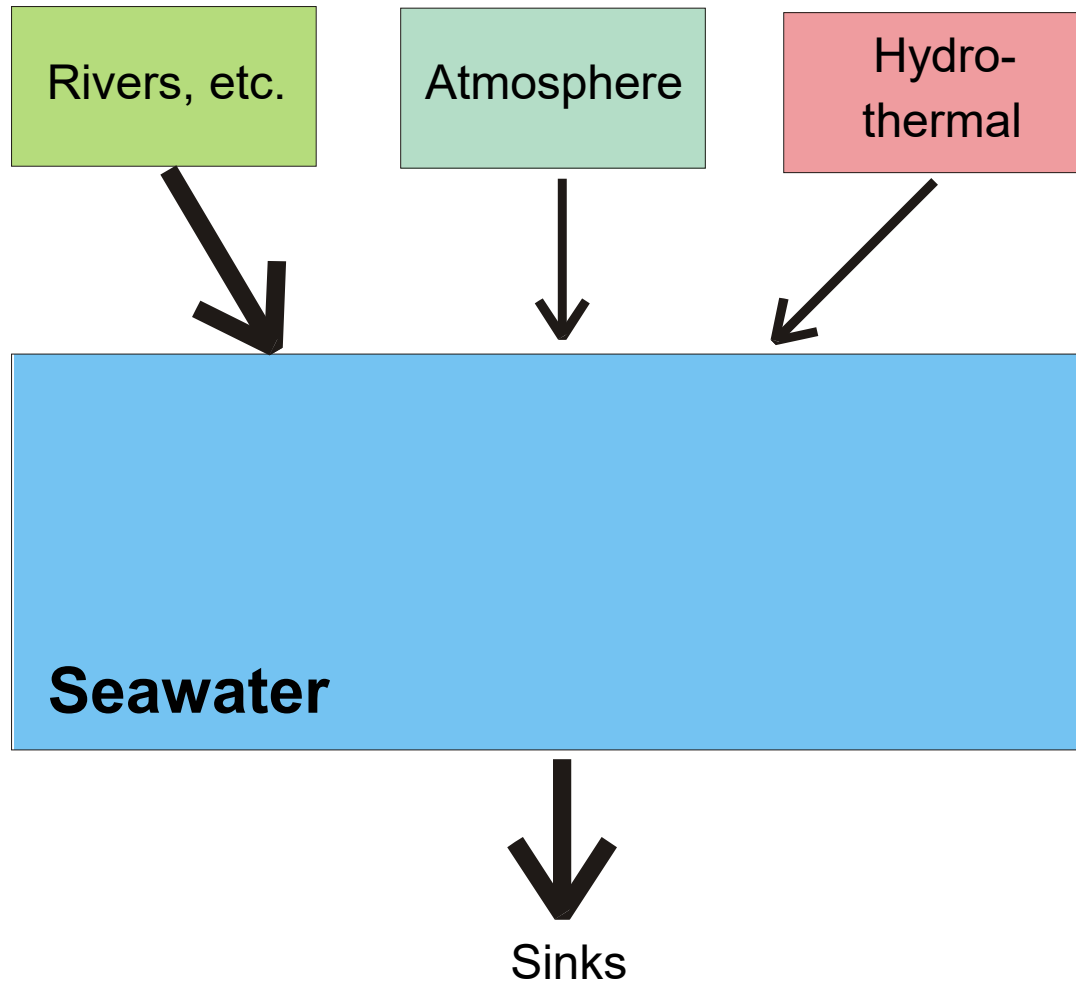




Why is the Sea Salty?



Sources AND sinks are important



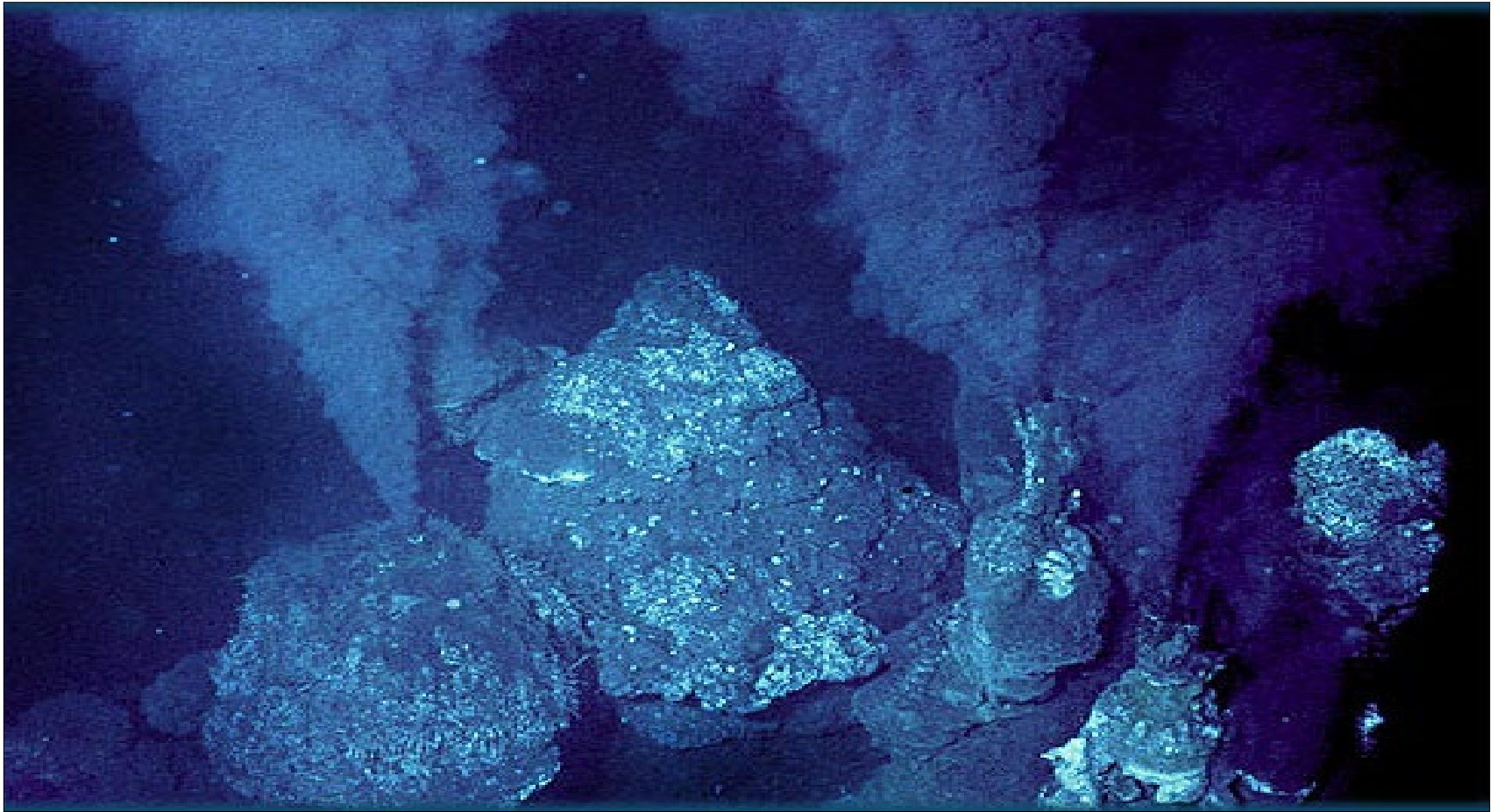
***Some sources are obvious:
e.g. rivers***



Mackenzie River, Canada

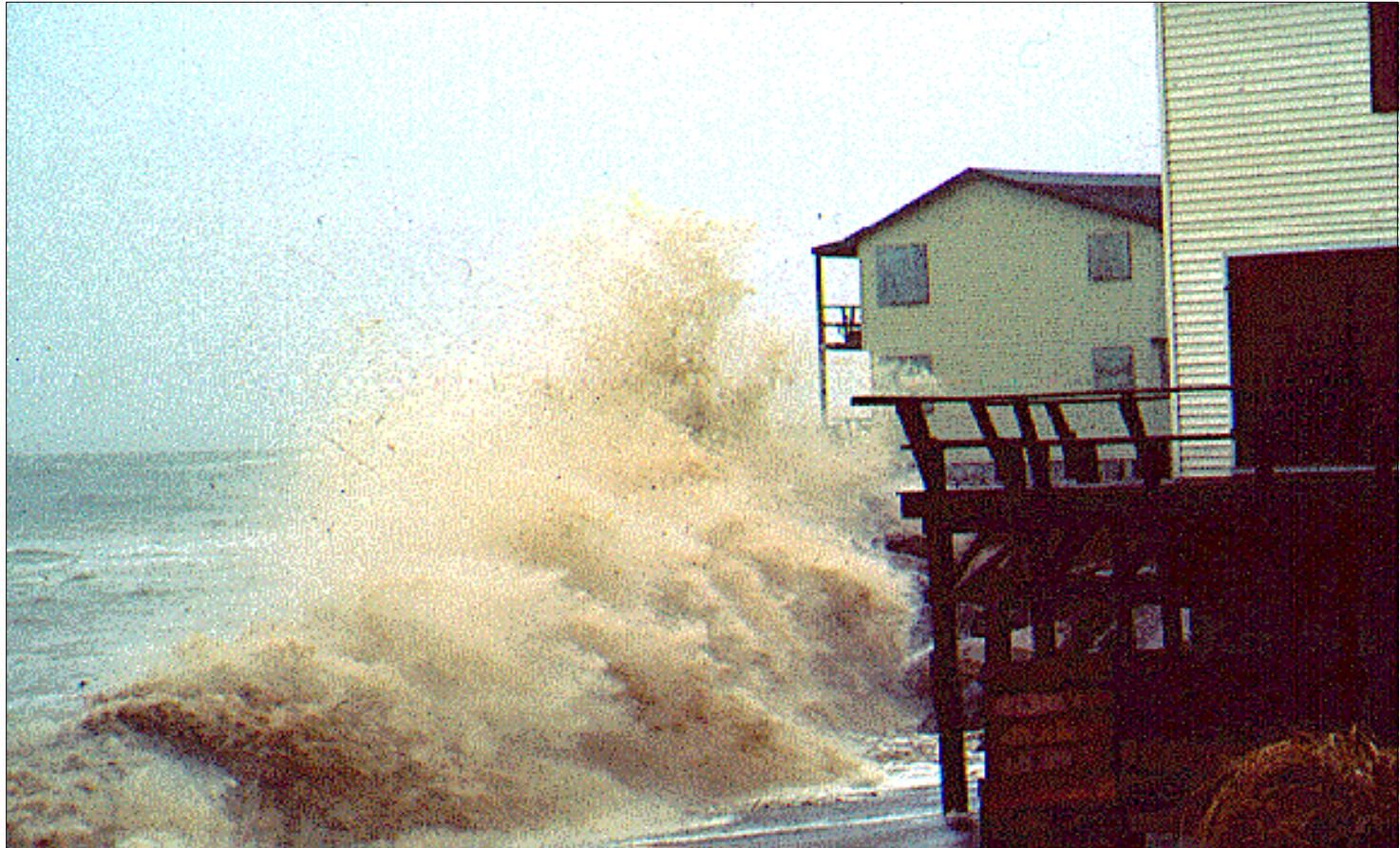


Hydrothermal Inputs





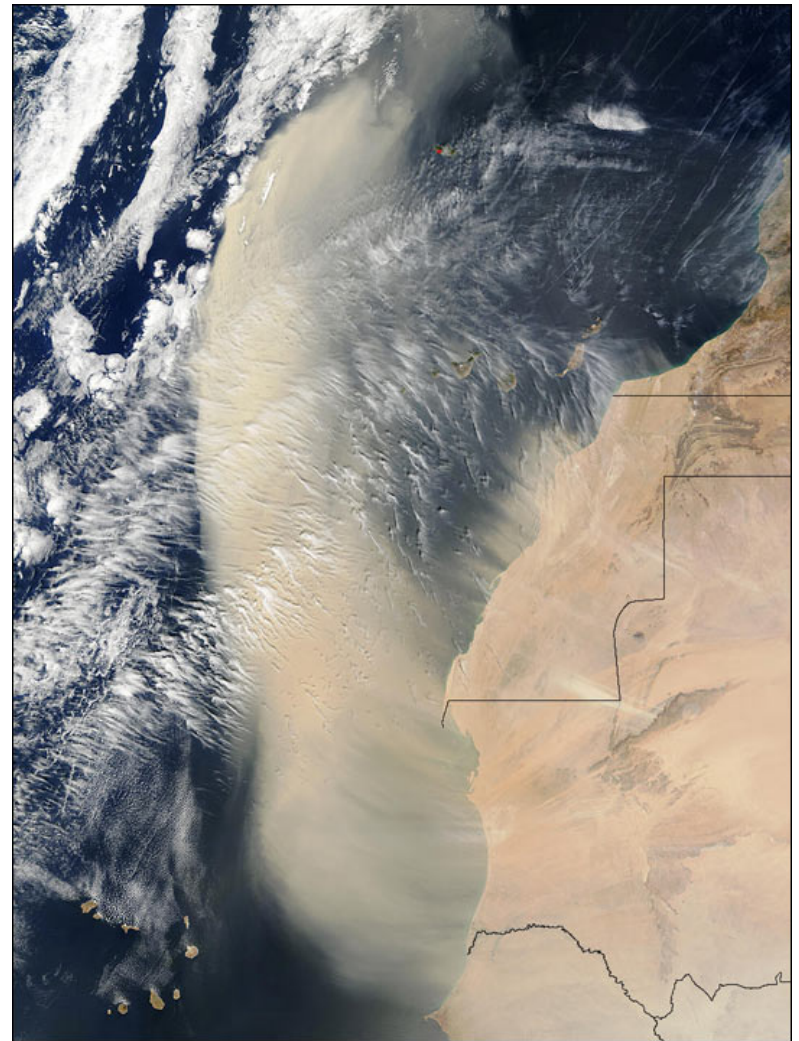
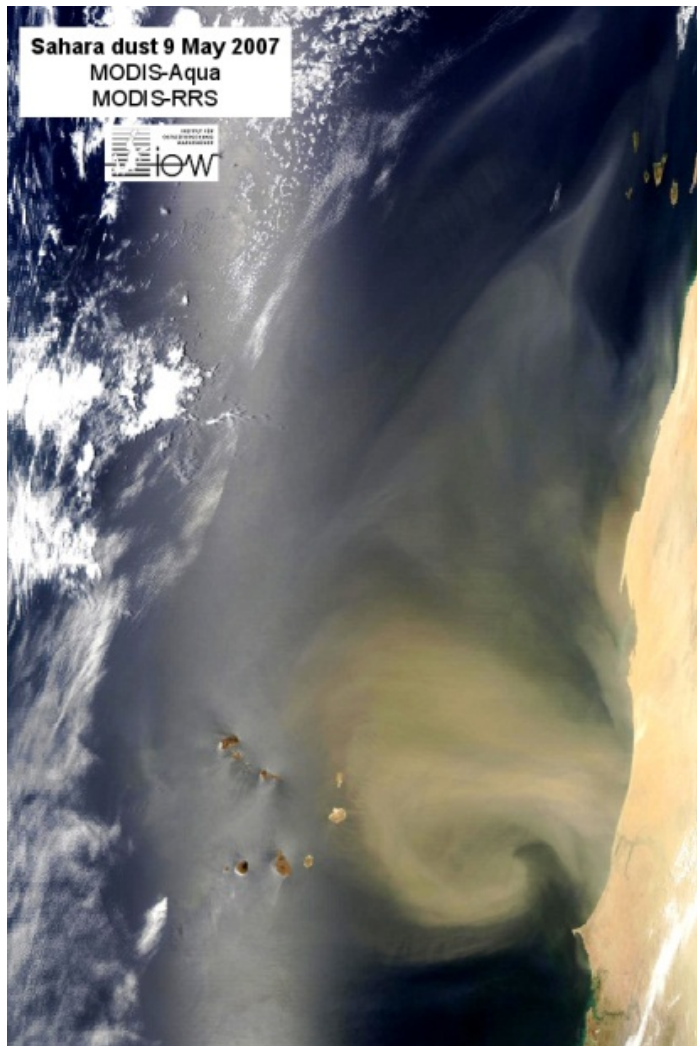
Coastal Erosion



Storm waves from a winter northeaster pound the beach at the base of two houses at Camp Ellis in Saco. In subsequent years both of these houses were destroyed by storms. Erosion in this area has exceeded 25 meters (82 ft) since 1950 and is expected to continue.



Some sources are only obvious when you have a good viewpoint



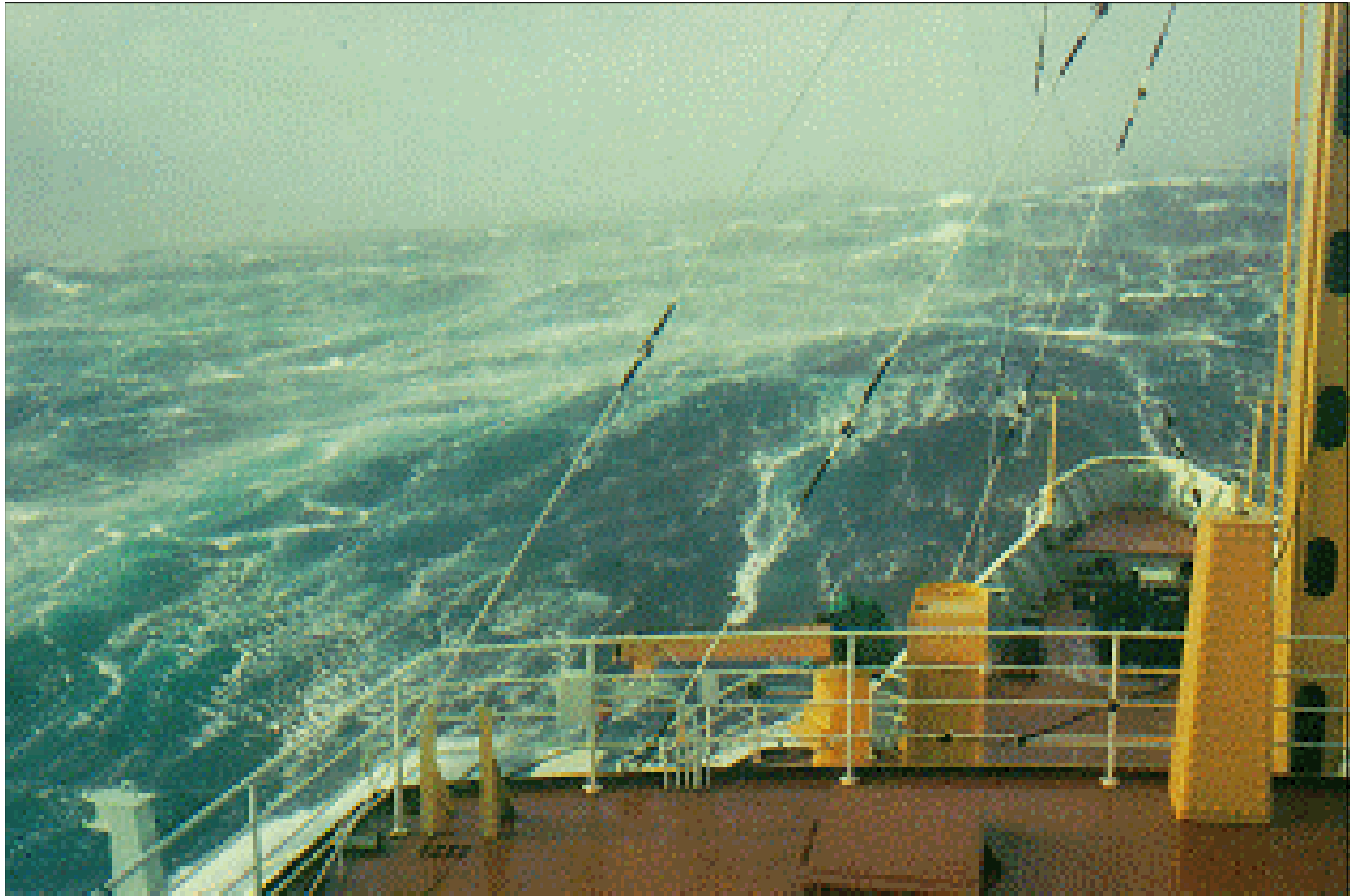


Some Sinks are Obvious





Some you have to think about...





Rain to River to Sea





Rainfall Chemistry

Two main sources for ions:

- Chemicals from particles (sea salt, dust, aerosols)



TABLE 3.4 Typical Concentrations of Major Ions in Continental and Marine Rainfall (in mg/l)

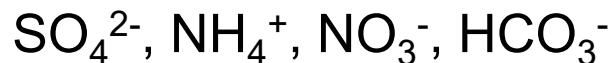
Ion	Continental Rain	Marine and Coastal Rain
Na^+	0.2–1	1–5
Mg^{++}	0.05–0.5	0.4–1.5
K^+	0.1–0.3 ^a	0.2–0.6
Ca^{++}	0.1–3.0 ^a	0.2–1.5
NH_4^+	0.1–0.5 ^b	0.01–0.05
H^+	pH = 4–6	pH = 5–6
Cl^-	0.2–2	1–10
SO_4^{--}	1–3 ^{2,b}	1–3
NO_3^-	0.4–1.3 ^b	0.1–0.5

^aIn remote continental areas; $\text{K}^+ = 0.02\text{--}0.07$; $\text{Ca}^{++} = 0.02\text{--}0.20$; $\text{SO}_4 = 0.2\text{--}0.8$

^bIn polluted areas; $\text{NH}_4^+ = 1\text{--}2$; $\text{SO}_4^{--} = 3\text{--}8$; $\text{NO}_3^- = 1\text{--}3$.

Sources: See Table 3.1.

- Chemicals from atmospheric gases (natural and pollution)



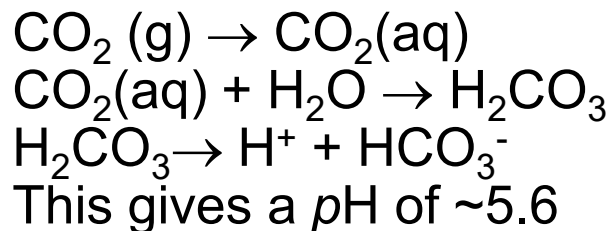


Rainfall and Weathering

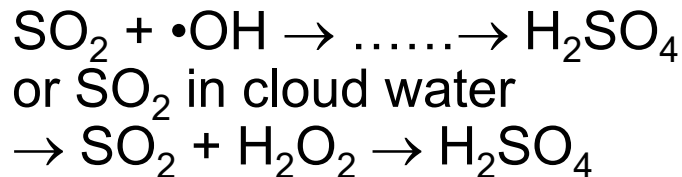
$\text{Cl}^- = \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+ > \text{Ca}^{2+} > \text{SO}_4^{2-} > \text{NO}_3^- = \text{NH}_4^+$
MARINE →→→→→→→→→→→→→→→CONTINENTAL

Rainfall is acidic!

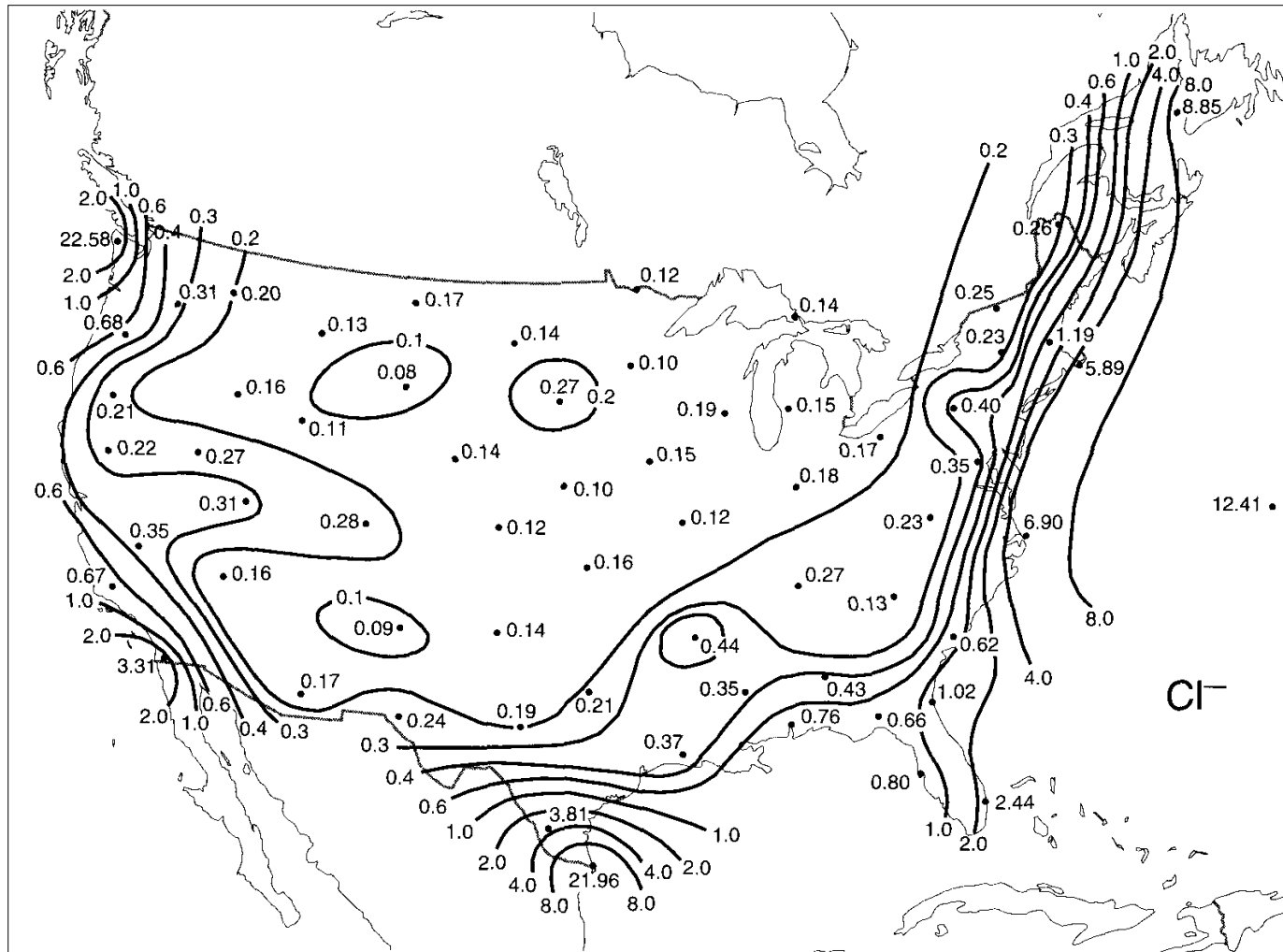
Natural



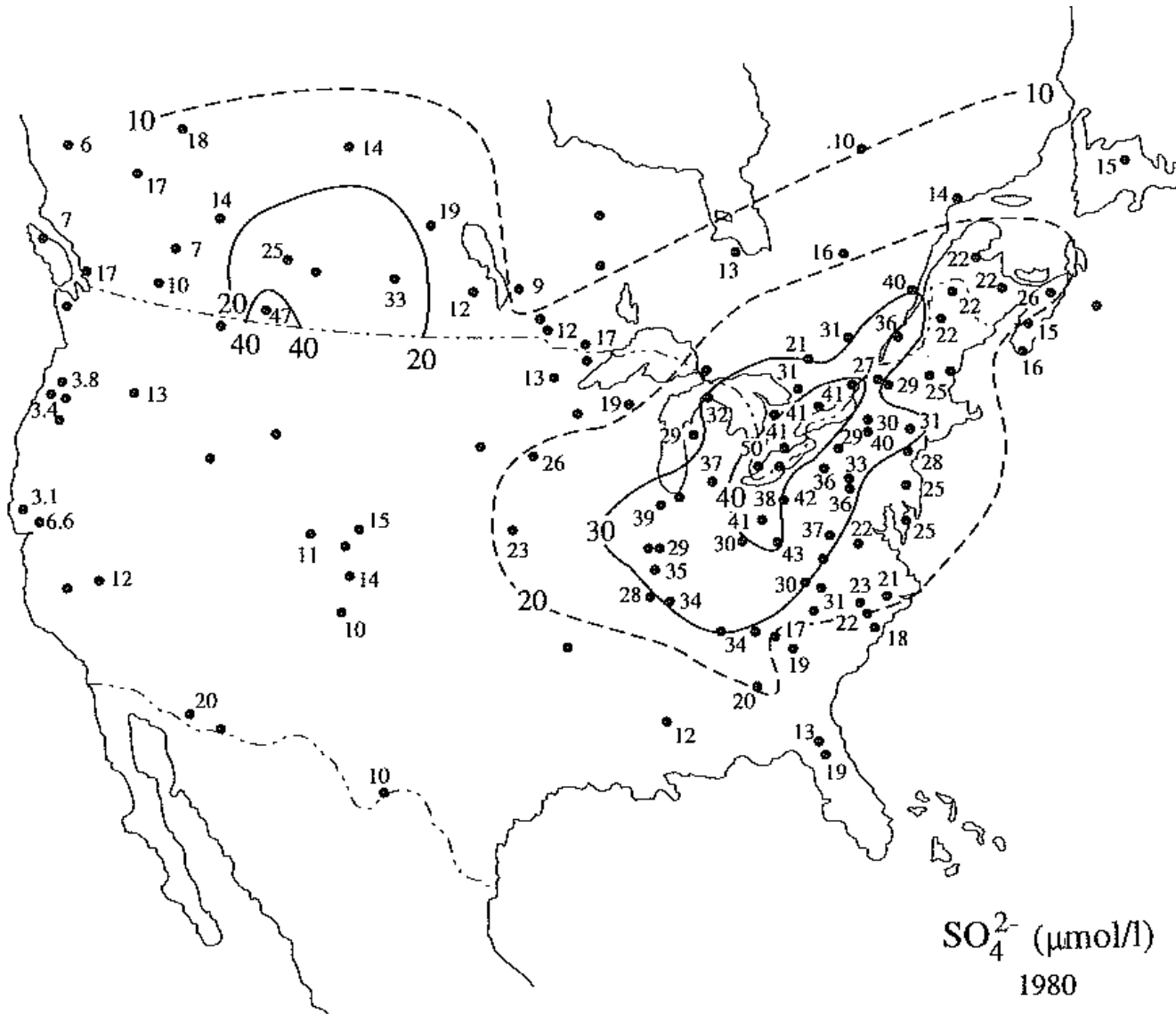
Pollution



Rainfall in polluted areas can have $pH < 4$ (average annual)



Distance from the coast affects Rainfall Chemistry



Distance from the coast affects Rainfall Chemistry

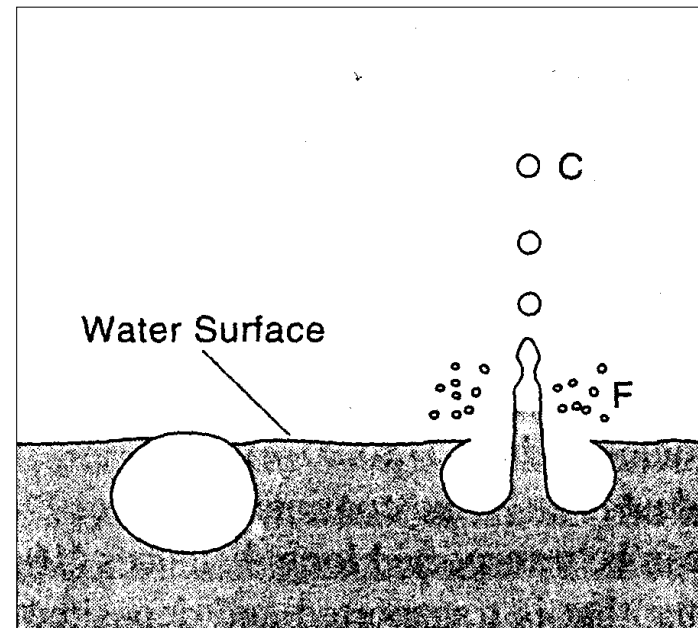


,Cyclic' salt

Sea-salt aerosol formation:

- buoyant bubble reaches sea surface and bursts
- water rushes in to fill void
- creates upward-moving jet which breaks apart
- creates about 10 droplets of seawater ejected to about 15cm height
- these evaporate: produce sea-salt particles (2 to 20 μm radius) (smaller particles produced from bubble film)

Composition is SIMILAR to sea-salt (may differ in trace components). Residence time for sea-salt in marine atmosphere is 3 days. Therefore can be transported considerable distances to land. About $100 \times 10^{12} \text{ g yr}^{-1}$ of sea-salt is deposited on continents .





Rain to River

Dissolved Material:

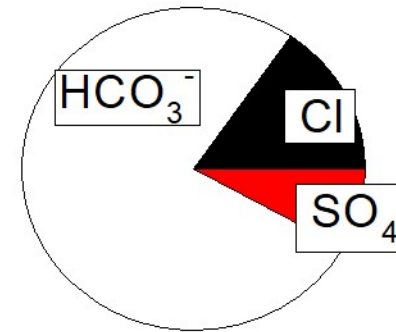
- Composition of dissolved salts in rivers is different than in rainfall

Concentration of dissolved salts in river > rain:

- effect of evaporation (2-3x)
- effect of weathering of rocks (10x)

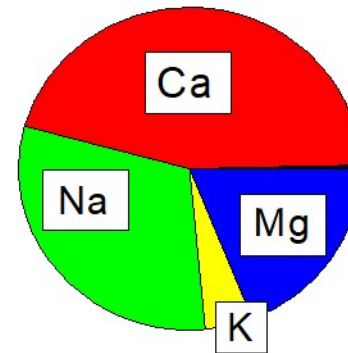
Suspended Material:

- total suspended river load $10\text{-}20 \times 10^{15} \text{ g yr}^{-1}$
- strongly impacted by humans
- = about 90% of the total material transport, BUT less important for marine chemistry
- enriched in insoluble elements (Al, Fe, Si) also Ca, Mg, Na, P

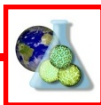


River Water
 $\text{TDS} = 0.1 \text{ g kg}^{-1}$

(20 x higher conc.
than Rainwater)

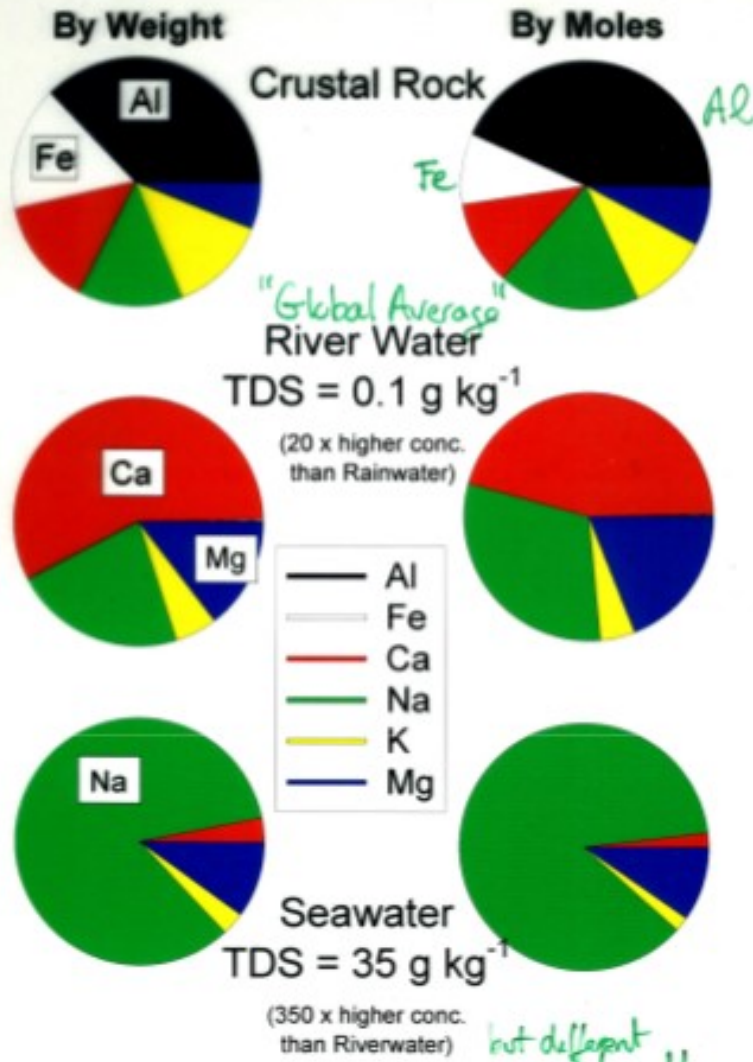


River Water Major Anion (top) and Cation (bottom) Composition (in moles)

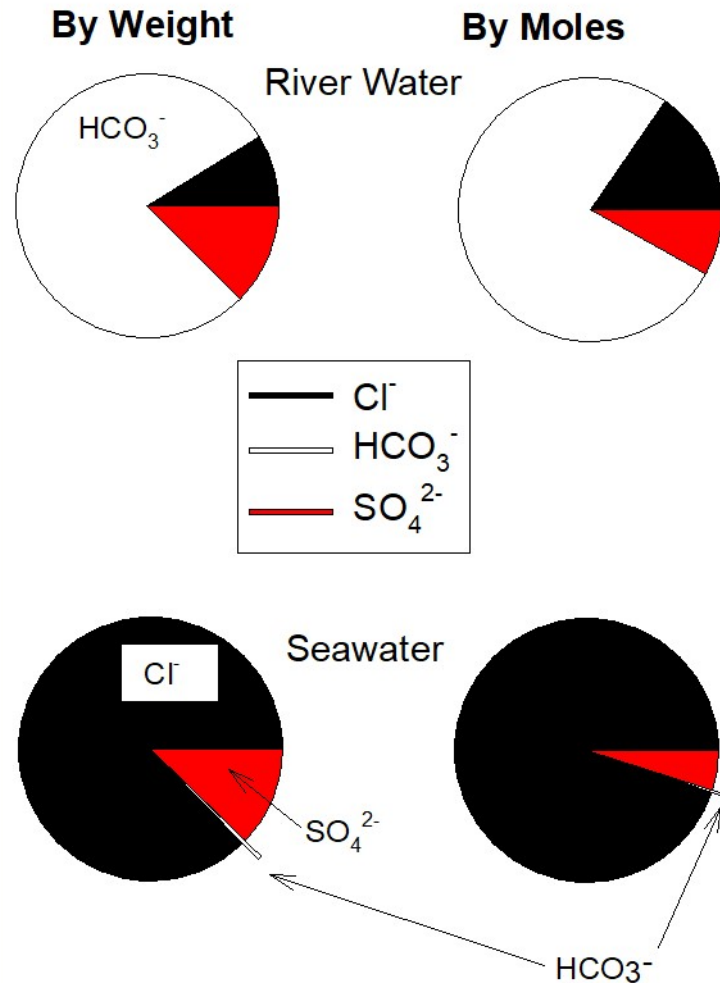


Crustal Rock and River Water

Major Cation Composition



Major Anion Composition





What gets into river water?

The abundance of an element in river water and partitioning between dissolved and particulate material depends on:

1. Abundance in the Earth's crustal rocks*
2. Chemical nature of the element/ion
3. Nature of weathering reactions including the composition of rainfall*
4. Biological processes in soils*
5. Human influence*

** varies regionally*



Chemical Weathering in Soils

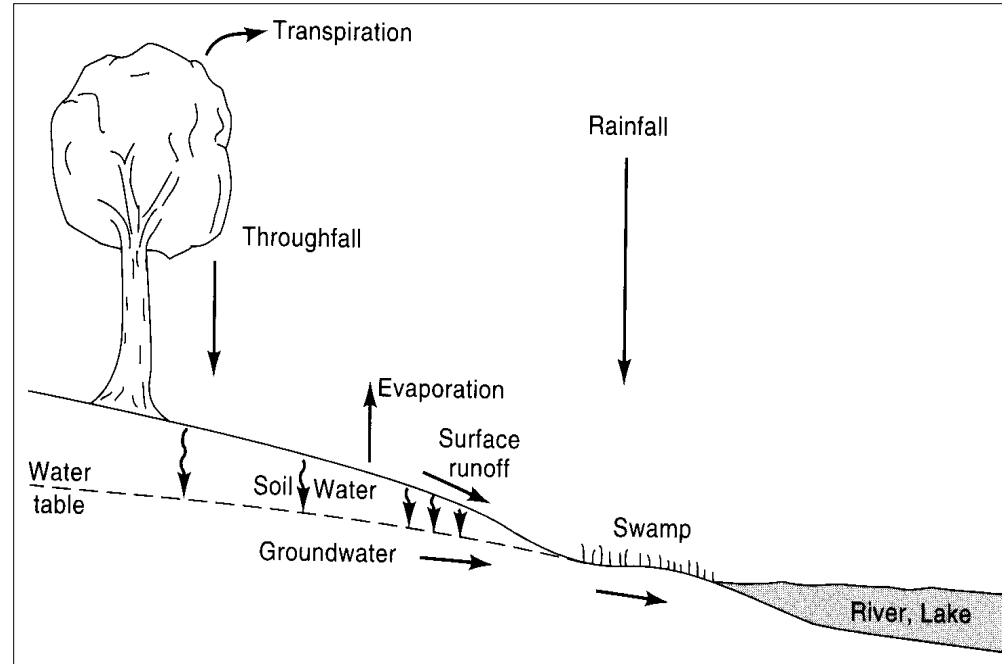
• Soil water becomes more acidic due to



(followed by dissociation of CO_2)

also

- oxidation of sulfide minerals to H_2SO_4
- dissolution of organic acids



Acidic rainfall and soil water reacts with rocks in surface water,
soil water and groundwater

→ dissolved minerals

some dissolved materials react to form ‘secondary minerals’

This is **‘Chemical Weathering’**

(compare with **‘Physical Weathering’**)



Chemical Weathering

TABLE 4.3 Common Primary Minerals That Undergo Weathering

Mineral	Generalized Composition	Weathering Rock Type(s)	Main Reaction
Olivine	$(\text{Mg,Fe})_2\text{SiO}_4$	Igneous	Oxid. of Fe Cong. diss. by acids
Pyroxenes	$\text{Ca}(\text{Mg,Fe})\text{Si}_2\text{O}_6$ or $(\text{Mg,Fe})\text{SiO}_3$	Igneous	Oxid. of Fe Cong. diss. by acids
Amphiboles	$\text{Ca}_2(\text{Mg,Fe})_3\text{Si}_8\text{O}_{22}(\text{OH})_2$ (also some Na and Al)	Igneous Metamorphic	Oxid. of Fe Cong. diss. by acids
Plagioclase feldspar	Solid solution between $\text{NaAlSi}_3\text{O}_8$ (albite) and $\text{CaAl}_2\text{Si}_2\text{O}_8$ (anorthite)	Igneous Metamorphic	Incong. diss. by acids
K-feldspar	KAlSi_3O_8	Igneous Metamorphic Sedimentary	Incong. diss. by acids
Biotite	$\text{K}(\text{Mg,Fe})_3(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$	Metamorphic Igneous	Incong. diss. by acids Oxid. of Fe
Muscovite	$\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$	Metamorphic	Incong. diss. by acids
Volcanic glass (not a mineral)	Ca,Mg,Na,K,Al,Fe-silicate	Igneous	Incong. diss. by acids and H_2O
Quartz	SiO_2	Igneous Metamorphic Sedimentary	Resistant to diss.
Calcite	CaCO_3	Sedimentary	Cong. diss. by acids
Dolomite	$\text{CaMg}(\text{CO}_3)_2$	Sedimentary	Cong. diss. by acids
Pyrite	FeS_2	Sedimentary	Oxid. of Fe and S
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Sedimentary	Cong. diss. by H_2O
Anhydrite	CaSO_4	Sedimentary	Cong. diss. by H_2O
Halite	NaCl	Sedimentary	Cong. diss. by H_2O

Note: cong. = congruent; incong. = incongruent; diss. = dissolution; oxid. = oxidation.

Chemical Weathering Mechanisms

Nature of reacting substance (H_2O , acids, O_2)

Congruent or incongruent dissolution

Congruent = Simple Dissolution (all products end up in solution)

Incongruent = dissolution plus some re-precipitation forms: Secondary Minerals



Where do the ions come from?

Chloride (Cl⁻)

- **Dissolution of halite (NaCl) from sedimentary rocks (57%)**
 $\text{NaCl (s)} \rightarrow \text{Na}^+ \text{ (aq)} + \text{Cl}^- \text{ (aq)}$
- **Pollution (about 30%)**
(Sewage, road salt, mining, etc.)
- **Sea salt deposition from atmosphere (13%)**
sea-salt contribution varies with location
→ distance from coast



Potassium (K⁺)

- **Acid weathering of silicate minerals (87%)**
minerals found in sedimentary, igneous and metamorphic rocks
(e.g. weathering of potassium feldspar (orthoclase)):
$$2 \text{KAlSi}_3\text{O}_8 + 2 \text{H}^+ + 9 \text{H}_2\text{O} \rightarrow \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2 \text{K}^+ + 4 \text{H}_4\text{SiO}_4$$
- **Pollution (7%)**
- **Cyclic Salt (about 1%)**
- **Dissolution of *evaporite* deposits, etc. (remainder)**



Calcium and Magnesium (Ca^{2+} and Mg^{2+})

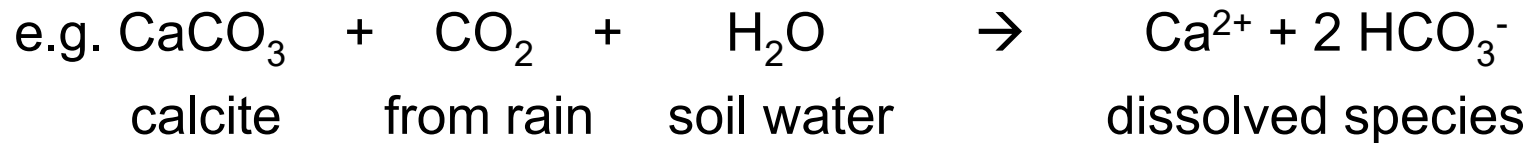
- **Weathering (90%)**
 - sedimentary rocks
 - almost all from (calcite CaCO_3 and dolomite $\text{CaMg}(\text{CO}_3)_2$)
(*see next section*)
 - a very little from CaSO_4
 - a little from Ca-silicates
- **Pollution (9%)**
- **Cyclic salt (1%)**

Bicarbonate (HCO_3^-)

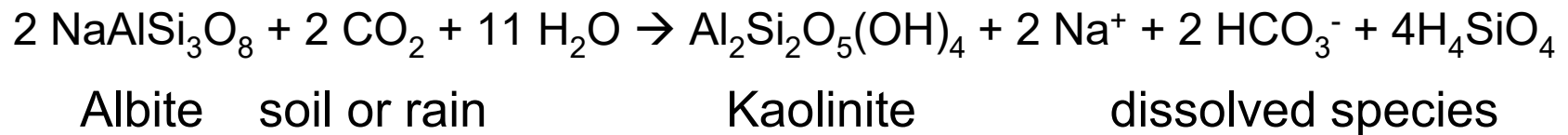
- **Weathering (98%)**
 - (the dissolution of limestone dominates river water chemistry).
- **Pollution (<2%)**
- **Cyclic sea salt (1%)**



Chemical Weathering and the Bicarbonate Ion



But bicarbonate can also be produced by chemical weathering of silicate minerals:



CO₂ is the acid supply for weathering.

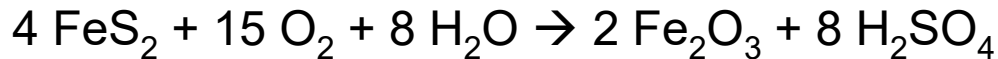
(Compare the source of C atoms in these two reactions.)



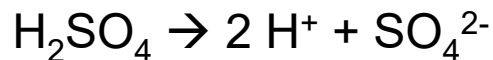
Chemical Weathering and the Bicarbonate Ion

Some HCO_3^- is also produced as a result of chemical weathering by other acids:

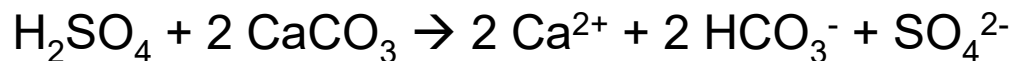
e.g.: oxidation of pyrite upon exposure to air produces sulfuric acid



then:



this acid can attack limestone:



Overall:

About 64 % of HCO_3^- in river water comes from the atmosphere

About 34 % comes from rock.



Sulfate (SO_4^{2-})

- **pollution about 54%**
- **weathering about 33%**
 - oxidation of pyrite (FeS_2)
 - weathering of gypsum and anhydrite (CaSO_4)
- **volcanic activity 8%**
- **cyclic salt (2%)**



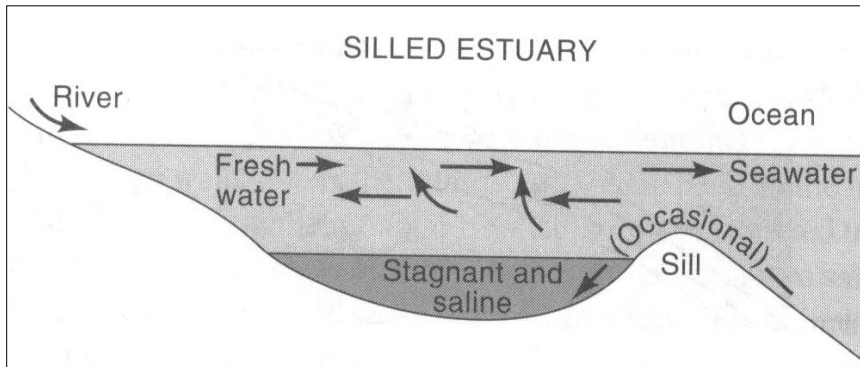
River to Sea

Special physico-chemical and biological processes can add or remove elements from riverwater and/or seawater within estuaries:

- Exchanges with sediments
- Biological activity
- Human activity
- Ion-exchange reactions on clay minerals (later)
- Ionic strength changes \Rightarrow aggregation of colloidal materials
- Changes in pH \Rightarrow speciation changes (solubility changes)
- Changes in O_2 levels \Rightarrow redox reactions



Types of Estuaries



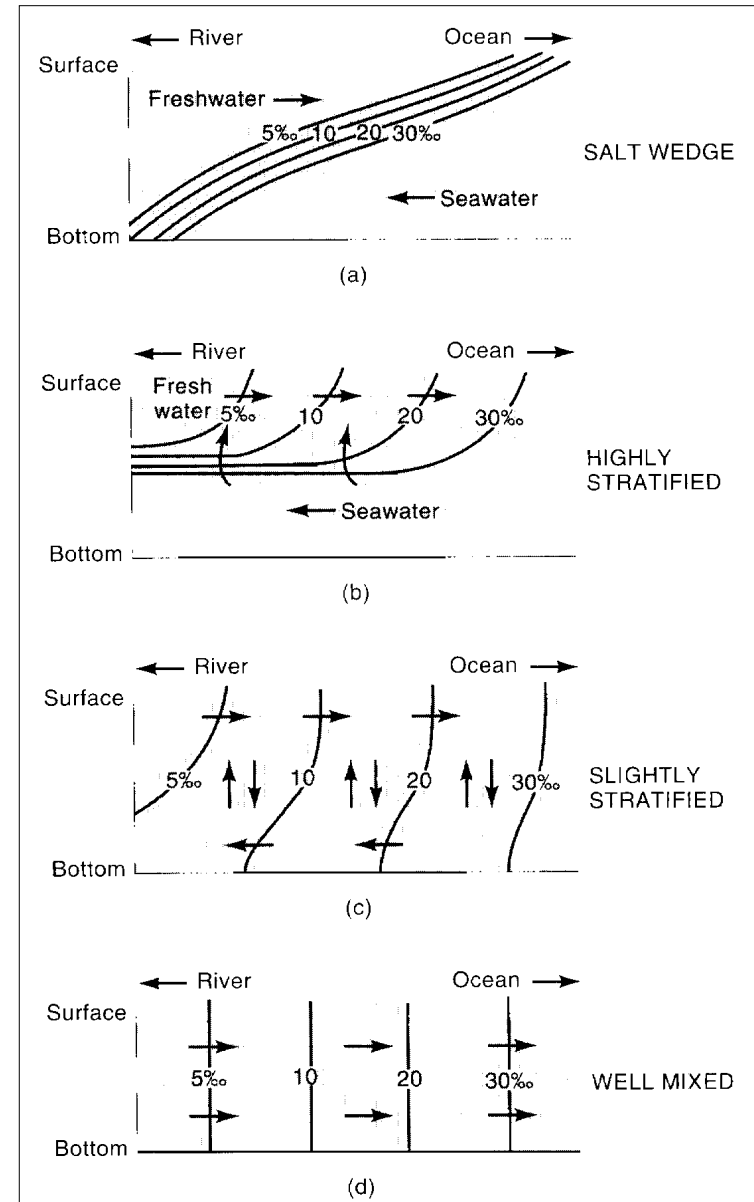
e.g. Baltic Sea, Black Sea, Mediterranean, etc...

How much time is there for processes to occur?

flushing time of an estuary: $\Rightarrow \tau = V_f / R$

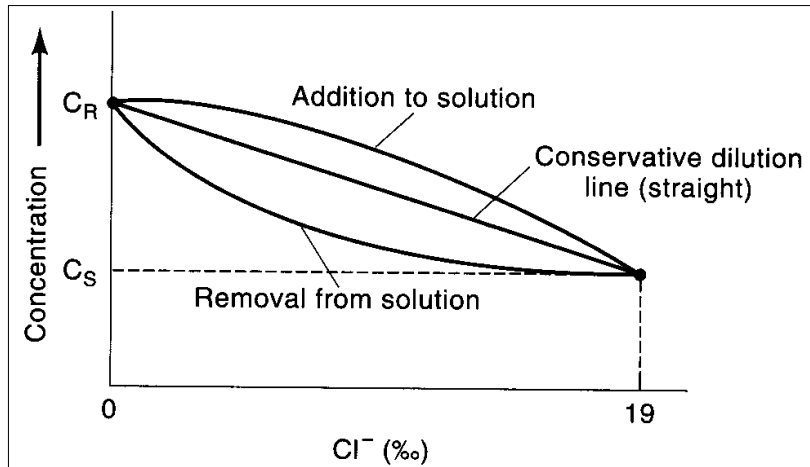
(where: V_f = volume of freshwater in the estuary, R is the river runoff)

Usually τ is several (1-10) days for 'normal' estuaries

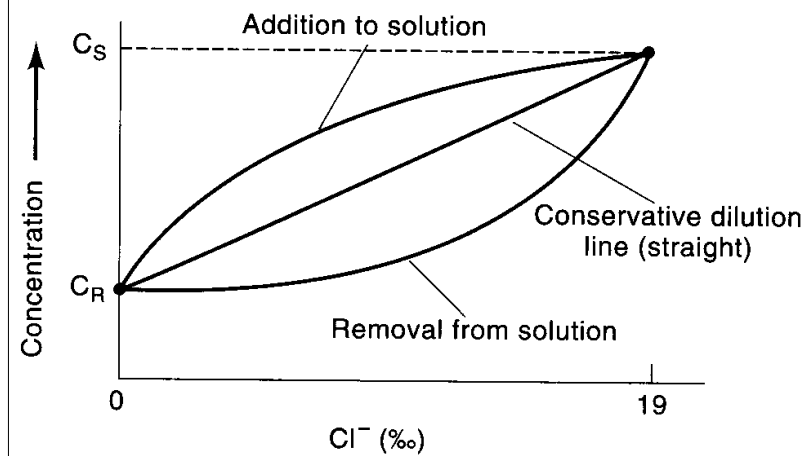




Addition and removal in estuaries: conservative vs. non-conservative mixing



(a)



(b)

