Lecture 17

Guest Lecturer this week. Prof. Greg Ravizza

- “Migrating Reservoirs” in the Hydrologic Cycle - Inorganic solubility examples from Rain and River chemistry

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Migrating Reservoirs” in the Hydrologic Cycle

We study rain and river compositions to learn about:

✓ how the cumulative effects of terrigenous weathering are superimposed on local watershed rain compositions.

✓ rates for material movement through the hydrosphere

✓ rates at which the land masses of earth are eroded

✓ anthropogenic effects.

Rain

Rain is the starting point composition for water in a given watershed. Rivers and ground water compositions in turn reflect weathering and biological processes, followed by anthropogenic effects.

For both rain and river water, dissolved solutes reflect the abundance of different types of solids in the environments and their solubility, both of which are highly variable.

Rain

Why does rain form?

The atmosphere becomes supersaturated in water vapor at local conditions of temperature and pressure

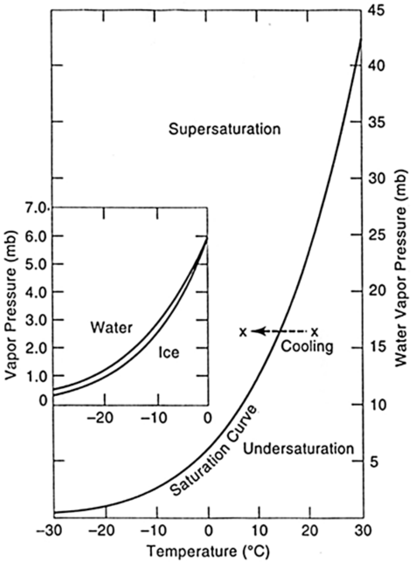


Figure 3.1. Saturation vapor pressure in millibars (1 mb = 10^3 dynes/cm^2) of pure water as a function of temperature (°C). The dashed arrow represents the change from undersaturation to supersaturation upon cooling of air with a constant water vapor pressure. Inset: Saturation vapor pressure (mb) over water ice at temperatures below 0°C. (After H.R. Byers, *Elements of Cloud Physics*. ©1965 by the University of Chicago Press. All rights reserved.)

Rain water delivers “new” water to a watershed. Its composition reflects

- ❖ fresh and weathered rocks of the watershed.
- ❖ natural and non-natural particulates in the atmosphere
- ❖ local gas fluxes to the atmosphere

Aerosols:

Rain drops form by nucleation on the surface of very fine (:m size) particles in the atmosphere called aerosols, which partly or completely dissolve.

Natural sources:	Marine	-sea salt
	Terrestrial	-dust -soils -volcanic emissions -pollen/other plant materials -smoke
non-Natural (Anthropogenic) sources:	industrial	-particulates/soot -automobile emissions -bakeries/restaurants
	agricultural	dust/soils -agricultural fertilizers

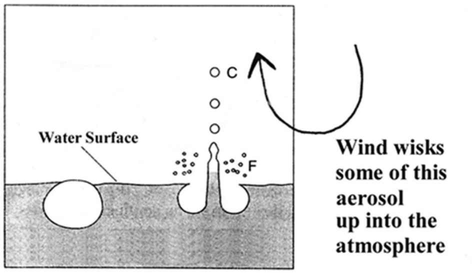


Figure 2.9. The formation of sea-salt particles from the bursting of bubbles. Large droplets originating from the jet are designated as C, whereas smaller particles produced from the bubble are designated as F. (After Junge 1963.)

Particulates/Aerosols are produced naturally by wind mobilization of fine components of terrigenous matter and by drying + mobilization of marine aerosols.

Only the small particles (F) are transported significant distances from their source.

Solid particulates contribute to rain in 2 distinct processes:

a. rainout	removal of particulates during droplet nucleation (occurs in clouds)
b. washout	removal of particulates as raindrops fall to the ground (occurs below

Surface Water Chemistry changes from rain to river:

river water has:

✶ a huge increase in SiO_2 and HCO_3^- (due to congruent dissolution of silicates and carbonates)

✶ a large increase in Ca (for same reasons)

✶ a relative deficit of K, due to retention in clays

✶ other ions have increased in concentration but their ratios to each other are similar to rain ratios.

Average North American rain and river water compared:

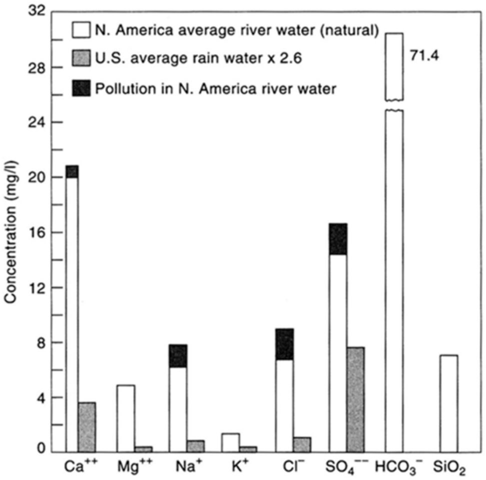


Figure 5.3. Comparison of dissolved composition of North American natural and polluted river water (data from Meybeck 1979) with U.S. rainwater (concentrations in mg/l). Rainwater concentrations are multiplied by 2.6 to correct for evaporation from the continents (see text).

source: Berner and Berner, Global Environment, 1996

Particulate control on global and local rain composition

Rain of dominantly marine or continental origins are distinct

The *mostly marine* ions are: Cl^- = Na^+ >Mg^{2+}

The *mostly terrigenous* ions are: $K^+ > Ca^{2+} > SO_4^{2-} > NO_3^{2-} = NH_4^+$, $Al^{+3} = SiO_2(aq)$

The presence of Al^{+3} or $SiO_2(aq)$ (both highly pH dependent) indicates continental origin for a rain water, but their proportions relative to other solutes are complicated, so they are not used to quantitatively source rain water.

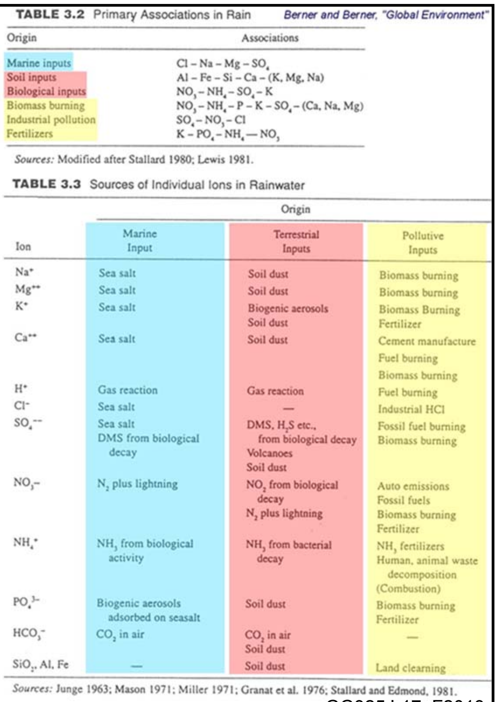


TABLE 3.2 Primary Associations in Rain

Berner and Berner, "Global Environment"

Origin	Associations
Marine inputs	Cl – Na – Mg – SO_4
Soil inputs	Al – Fe – Si – Ca – (K, Mg, Na)
Biological inputs	NO_3 – NH_4 – SO_4 – K
Biomass burning	NO_3 – NH_4 – P – K – SO_4 – (Ca, Na, Mg)
Industrial pollution	SO_4 – NO_3 – Cl
Fertilizers	K – PO_4 – NH_4 — NO_3

Sources: Modified after Stallard 1980; Lewis 1981.

TABLE 3.3 Sources of Individual Ions in Rainwater

	Origin		
Ion	Marine Input	Terrestrial Inputs	Pollutive Inputs
Na^+	Sea salt	Soil dust	Biomass burning
Mg^{++}	Sea salt	Soil dust	Biomass burning
K^+	Sea salt	Biogenic aerosols Soil dust	Biomass Burning Fertilizer
Ca^{++}	Sea salt	Soil dust	Cement manufacture Fuel burning Biomass burning
H^+	Gas reaction	Gas reaction	Fuel burning
Cl^-	Sea salt	—	Industrial HCl
SO_4^{--}	Sea salt DMS from biological decay	DMS, H_2S etc., from biological decay Volcanoes Soil dust	Fossil fuel burning Biomass burning
NO_3^-	N_2 plus lightning	NO_2 from biological decay N_2 plus lightning	Auto emissions Fossil fuels Biomass burning Fertilizer
NH_4^+	NH_3 from biological activity	NH_3 from bacterial decay	NH_3 fertilizers Human, animal waste decomposition (Combustion)
PO_4^{3-}	Biogenic aerosols adsorbed on seasalt	Soil dust	Biomass burning Fertilizer
HCO_3^-	CO_2 in air	CO_2 in air Soil dust	—
SiO_2, Al, Fe	—	Soil dust	Land clearning

Sources: Junge 1963; Mason 1971; Miller 1971; Granat et al. 1976; Stallard and Edmond, 1981.

Particulate control on global and local rain composition

✓ Marine aerosols formed from drying of sea water dominate rain compositions over the oceans, coasts and islands like Hawaii.

✓ These aerosols contain the major sea water ions in the same proportion as they occur in the oceans.

✓ The marine component is rained out progressively with distance from the coast.

✓ Compositions become more terrestrial towards the centers of large land masses as more ions are derived from terrigenous materials.

Pollution in Rain

After isolating the likely marine input, the remainder is considered to be a combination of:

✓ local terrigenous components
✓ anthropogenic components

Both are dominated by local effects and can be perturbed by human activities, such as:

✓ land cultivation
✓ industrial activities
✓ general urbanization

The Pollutive component can be:

✓ "more than normal" amounts of ions in otherwise natural proportions
✓ more ions in some other proportion.
✓ ions or molecules not naturally observed

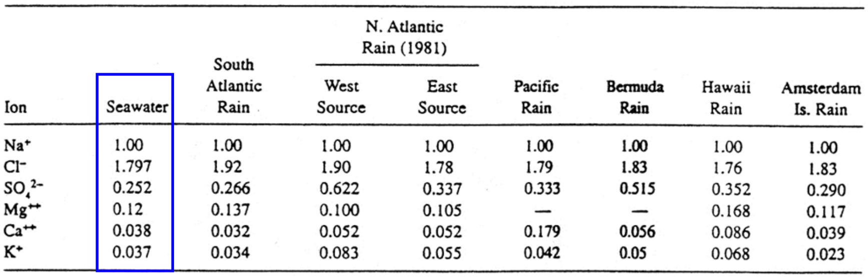
Except for Ca, all the other major ions of sea water behave conservatively (elemental ratios are constant throughout the oceans).

We use ions such as Cl^- and Na^+, to determine the amount of marine aerosol dissolved in rainwater, since they have almost no non-marine natural sources.

These then are a good starting point for understanding the sources of other ions in a particular rain water.

Note the similarities, particularly for Cl^-/Na^+ ratio of various marine rains

TABLE 3.5 Major Element Composition, in Terms of Weight Ratios to Na^+, for Seawater and Marine and Island Rains *(ion concentrations are ratioed to Na^+, although I prefer ratios to Cl^-).*



Ion	Seawater	South Atlantic Rain	N. Atlantic Rain (1981) West Source	N. Atlantic Rain (1981) East Source	Pacific Rain	Bermuda Rain	Hawaii Rain	Amsterdam Is. Rain
Na^+	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Cl^-	1.797	1.92	1.90	1.78	1.79	1.83	1.76	1.83
SO_4^{2-}	0.252	0.266	0.622	0.337	0.333	0.515	0.352	0.290
Mg^{++}	0.12	0.137	0.100	0.105	—	—	0.168	0.117
Ca^{++}	0.038	0.032	0.052	0.052	0.179	0.056	0.086	0.039
K^+	0.037	0.034	0.083	0.055	0.042	0.05	0.068	0.023

Each other constituent of rain can be compared to the Cl^- content to determine excesses or deficits relative to marine components.

Excesses or deficits can be understood by looking at:

- ❖ the proportion of the ion added
- ❖ the potential terrigenous particulate sources
- ❖ the governing solubility reactions involved
- ❖ considering non-marine anthropogenic sources of Cl^- from industrial inputs and road salting in cold regions.

$$\frac{[ion]}{[Cl^-]} \text{ (sea water ratio in g/g)} \times [Cl^-] \text{ (in weight units)} = [ion] \text{ (from sea water)}$$

[total ion] - [ion] (from sea water) = [ion] (non-marine)

☺ if [ion](non-marine) >1 there is an excess

☻ if [ion](non-marine) <1 there is a deficit (or excess Cl^-)

The strong rainout gradient for the marine component is easy to see in a contour map of Cl^- concentration in rain over 1 year over the continental US .

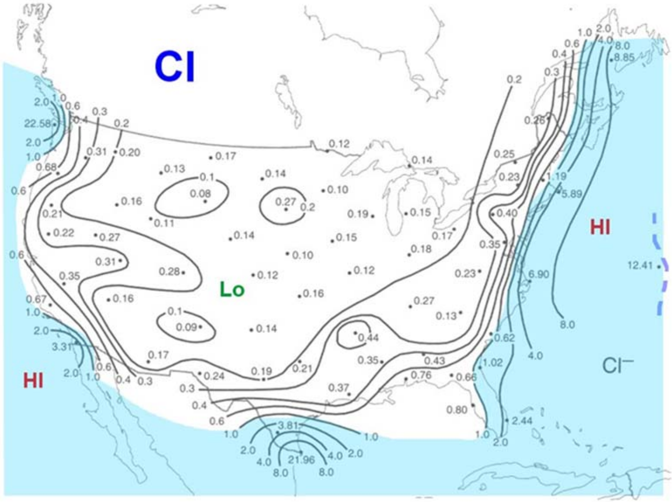


Figure 3.3. Average Cl⁻ concentration (mg/l) in rain over the United States, July 1955–June 1956. [After C. E. Junge and R. T. Werby, "The Concentration of Chloride, Sodium, Potassium, Calcium and Sulfate in Rainwater over the United States," *Journal of Meteorology* 15 (October 1958): 418, © 1958 by the American Meteorological Society.]

Berner and Berner, "Global Environment"

Na^+ distribution is more (next page) complicated.

Comparing Na^+/Cl^-_{rain} to $Na^+/Cl^-_{seawater}$ shows **slight "excess" Na everywhere**.

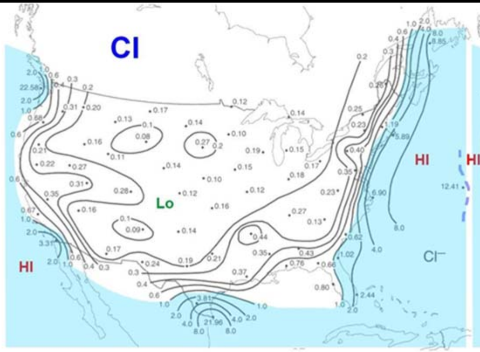
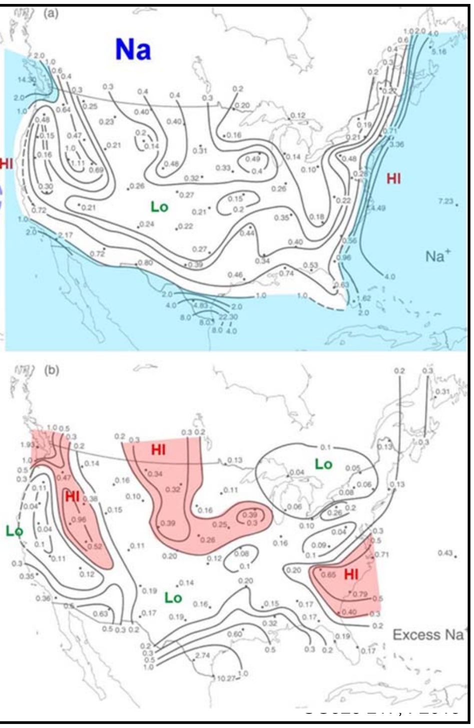


Figure 3.3. Average Cl⁻ concentration (mg/l) in rain over the United States, July 1955–June 1956. [After C. E. Junge and R. T. Werby, "The Concentration of Chloride, Sodium, Potassium, Calcium and Sulfate in Rainwater over the United States," *Journal of Meteorology* 15 (October 1958): 418, © 1958 by the American Meteorological Society.]

Berner and Berner, "Global Environment"

Figure 3.5. Dissolved Na⁺ (in mg/l) in continental United States rainfall, June 1955–June 1956. (a) Average Na⁺ concentration. (b) Average excess Na⁺ concentration, calculated as the difference between measured values shown in (a) and the values expected for seawater Cl⁻/Na⁺ ratios and the Cl⁻ concentrations shown in Figure 3.3. [After C. E. Junge and R. T. Werby, "The Concentration of Chloride, Sodium, Potassium, Calcium and Sulfate in Rainwater over the United States," *Journal of Meteorology* 15 (October 1958): 418, 420, © 1958 by the American Meteorological Society.]



Large Na excesses occur near regions where dust/soils/clays add Na^+ to the marine component. **The farther inland one gets, the easier it is to produce "excess" Na since the absolute Cl^- content is much lower.**

The more complex continental US: [Ca^{2+}] map derives mostly from $CaCO_3$ and $CaSO_4$ dissolution.

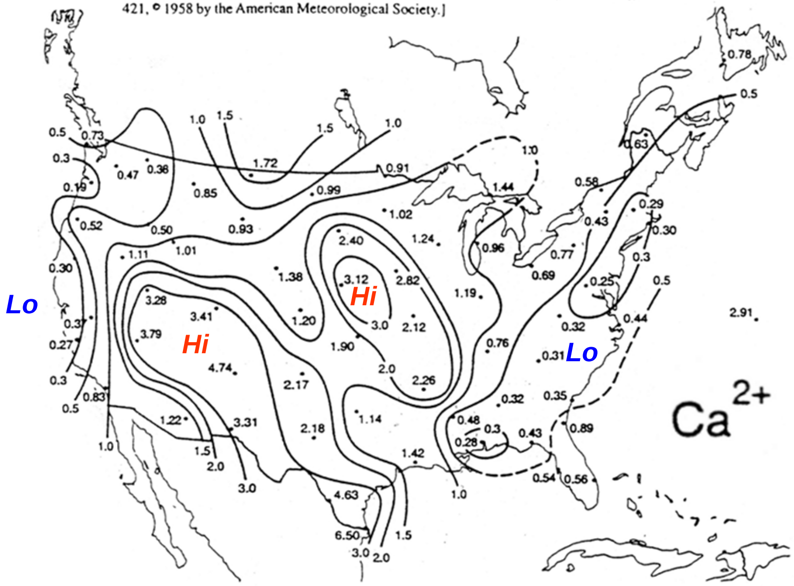


Figure 3.6. (a) Dissolved Ca^{2+} concentrations (in mg/l) in rainwater over the continental United States. June 1955–June 1956 [After C. E. Junge and R. T. Werby, "The Concentration of Chloride, Sodium, Potassium, Calcium and Sulfate in Rainwater over the United States," *Journal of Meteorology* 15 (October 1958): 421, © 1958 by the American Meteorological Society.]

Calcium in US rain.

After subtracting the small marine component using $Ca/Cl_{\text{sea water}}$, the rest of the Ca is sourced by comparing Ca content, rain pH and SO_4^{2-}.

- ❖ $CaCO_3$ dissolution neutralizes rain acidity, raising pH.
- ❖ $CaSO_4$ dissolution does not affect pH.

$CaCO_3$ is the dominant source of Ca in most continental rain waters. We can tell this because high [Ca^{2+}] is usually accompanied by slightly higher pH.

Exceptions are in arid regions (e.g., southwestern US), where $CaSO_4$ is prevalent in dry lake beds and soils.

$CaSO_4$ particles add Ca to rain without the base CO_3^{2-}, so that pH is not shifted as [Ca^{2+}] increases along with [SO_4^{2-}].

We must take care to distinguish high sulfate from this process as opposed to sulfate that is high from SO_3 addition to produce "acid rain".

Rain summary:

We can then understand the "starting" composition of water that enters a particular watershed by isolating ●marine, ● local terrigenous and ● anthropogenic components. *The farther from the coast, the less marine component to the rain.*

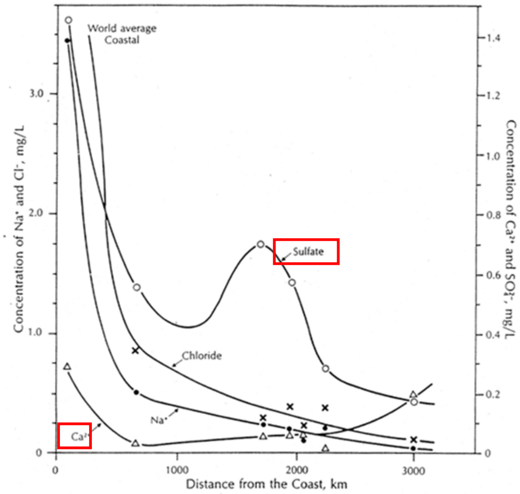


Figure 21.3 Variation of the major cations and anions in rainwater of the Amazon basin with distance from the Atlantic Ocean. The data for the Amazon basin in Table 21.2 are from Stallard and Edmond (1981) as compiled by Berner and Berner (1987).

Example from the Amazon Basin: Concentrations of all rain components drop with distance from the coast, reflecting rainout of marine particulates as storm clouds move inland.

Terrigenous components such as SO_4^{2-} and Ca^{2+} increase at various points further inland. The terrigenous component is dominated by local effects and can be perturbed by human activities (resulting in "more than normal" amounts of ions in otherwise natural proportions or more ions in some other proportion.

Rivers

Rivers reflect the net integrated effects over a watershed of meteoric water interactions with solids in that environment.

Rivers transport material in ***suspended*** and ***dissolved*** forms. These two materials are necessarily directly related in a particular river.

TDS (dissolved solids) chemistry reflects input from:

- inorganic reactions
- biological processes
- various water sources
  - rain
  - ground water discharge
  - lake discharge

Suspended load is mostly independent of watershed discharge rate. Instead it reflects:

- watershed basin relief (river gradient=Δheight/ Δdistance)

Basin relief reflects average time since last local orogeny and local rock type.

Younger and steeper mountains have rivers with mostly higher suspended load and have high erosion rates.

- watershed basin area
- rock type
- temperature

TABLE 5.1 Major Rivers that Flow to the Sea, Listed in Order of Discharge *Source: Berner and Berner, Global Environment, 1996*

		Annual Discharge				
River	Location	Water (km³/yr)	Dissolved Solids (Tg/yr)	Suspended Solids (Tg/yr)	Dissolved/ Suspended ratio	Drainage Area (10^6 km²)
1. Amazon	S. America	6300	275	1200	0.23	6.15
2. Zaire (Congo)	Africa	1250	41	43	0.95	3.82
3. Orinoco	S. America	1100	32	150	0.21	0.99
4. Yangtze (Chiang)	Asia (China)	900	247	478	0.53	1.94
5. Brahmaputra	Asia	603	61	540	0.11	0.58
6. Mississippi	N. America	580	125	210 (400)	0.6	3.27
7. Yenisei	Asia (Russia)	560	68	13	5.2	2.58
8. Lena	Asia (Russia)	525	49	18	2.7	2.49
9. Mekong	Asia (Vietnam)	470	57	160	0.36	0.79
10. Ganges	Asia	450	75	520	0.14	0.975
11. St. Lawrence	N. America	447	45	4	11.3	1.03
12. Parana	S. America	429	16	79	0.2	2.6
13. Irrawaddy	Asia (Burma)	428	92	265	0.35	0.43
15. Mackenzie	N. America	306	64	42	1.5	1.81
17. Columbia	N. America	251	35	10 (15)	3.5	0.67
20. Indus	Asia (India)	238	79	59 (250)	1.3	0.975
Red (Hungho)	Asia (Vietnam)	123	?	130	?	0.12
Huanghe (Yellow)	Asia (China)	59	22	1100	0.02	0.77

Lots of water

Lots of dissolved load

Lots of sediment

Not much sediment

Note: Tributaries are excluded. Tg = 10^6 tons = 10^{12} g.

Sources: Water and suspended solids from Milliman and Meade (1983) and Milliman and Syvitski (1992). Dissolved solids calculated from Table 5.7 and Pinet and Souriau (1988) (for the Irrawaddy). Suspended load values in parentheses indicate pre-dam values.

Suspended load variations around the globe:

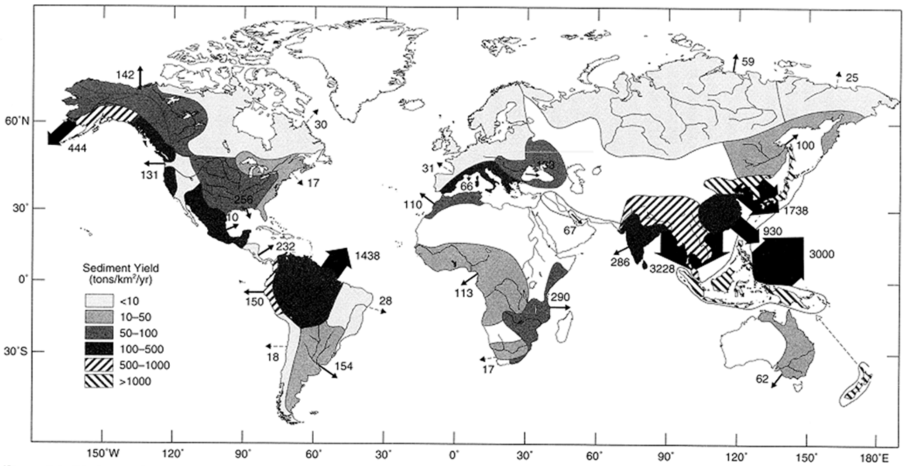


Figure 5.1. Discharge of suspended sediment from world drainage basins (in 10^6 tons/yr) as indicated by arrows. Sediment yield (tons/km²/yr) for various drainage basins is also shown by appropriate pattern (see legend). Open pattern indicates essentially no sediment discharges to the oceans. [After J. D. Milliman and R. H. Meade. "World-Wide Delivery of River Sediment to the Oceans," *Journal of Geology* 91(1): 16. Copyright © 1983 by The University of Chicago Press, reprinted by permission of the publisher.]

source: Berner and Berner, Global Environment, 1996

Human effects on sediment load

❖ increased erosion due to agriculture

❖ increased erosion due to deforestation

❖ decreased load transport due to dams

❖ decreased load transport due bank stabilization

❖ increased surface runoff due to urbanization (which also decreases groundwater recharge).

Sources of major ions in river water

Table 5.11 Sources of Major Elements in World River water (in Percent Actual Concentrations)
source: Berner and Berner, Global Environment (1996)

Element	Atmos. Cyclic Salt	Weathering			Pollution[b]
		Carbonates	Silicates	Evaporites[a]	
Ca	0.1	65	18	8	9
C (HCO_3^-)	<<1	61[c]	37[c]	0	2
Na	8	0	22	42	28
Cl	13	0	0	57	30
S (sulfate)	2[d]	0	0	22[d]	54
Mg	2	36	54	<<1	8
K	1	0	87	5	7
SiO_2 (aq)	<<1	0	99+	0	0

a. also includes NaCl from shales and thermal springs
b. values from Meybeck (1979) except sulfate, which is based on a calculation given in the text
c. for carbonates, 34% from calcite and doliomite and 27% from soil CO_2; for silicates, all 37% from soil CO_2; thus, total HCO_3^- from soil (atmospheric) CO_2 = 64% (see also Table 5.13)
d. other sources of river sulfate: natural biogenic emissions to atmosphere delivered to land, 3%; volcanism, 8%; pyrite weathering, 11%

The weathering and cyclic salt columns probably contain no real surprises to you (although cyclic salt estimates vary enormously in the literature)

The pollution column may seem striking.

These estimates rely on making a budget for riverine TDS from suspected natural sources, and then accounting for any "excesses" as pollutant inputs.

Solids Controls on river composition

Riverine Dissolved load reflects

- local precipitation
- climate
- the extent of local weathering
- ion solubility at various conditions:
  - T
  - pH
  - TOC (total organic carbon).

Suspended load reflects

- rock type
- climate

the suspended load is mostly composed of:

- weathering-resistant minerals (which can contain both high and low solubility elements)
- low solubility elements in secondary minerals
- organic particulates

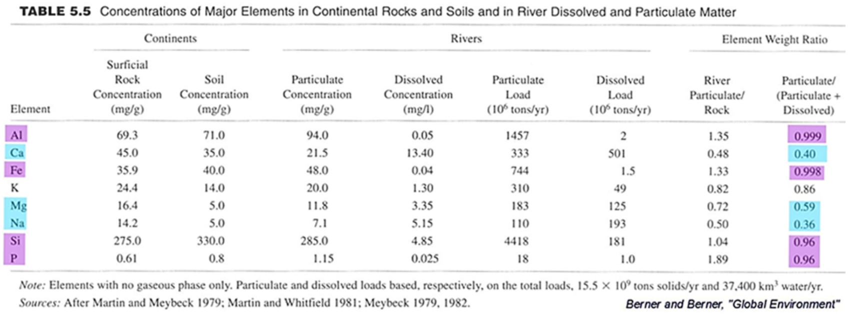


TABLE 5.5 Concentrations of Major Elements in Continental Rocks and Soils and in River Dissolved and Particulate Matter

Element	Continents		Rivers				Element Weight Ratio	
	Surficial Rock Concentration (mg/g)	Soil Concentration (mg/g)	Particulate Concentration (mg/g)	Dissolved Concentration (mg/l)	Particulate Load (10^6 tons/yr)	Dissolved Load (10^6 tons/yr)	River Particulate/ Rock	Particulate/ (Particulate + Dissolved)
Al	69.3	71.0	94.0	0.05	1457	2	1.35	0.999
Ca	45.0	35.0	21.5	13.40	333	501	0.48	0.40
Fe	35.9	40.0	48.0	0.04	744	1.5	1.33	0.998
K	24.4	14.0	20.0	1.30	310	49	0.82	0.86
Mg	16.4	5.0	11.8	3.35	183	125	0.72	0.59
Na	14.2	5.0	7.1	5.15	110	193	0.50	0.36
Si	275.0	330.0	285.0	4.85	4418	181	1.04	0.96
P	0.61	0.8	1.15	0.025	18	1.0	1.89	0.96

Note: Elements with no gaseous phase only. Particulate and dissolved loads based, respectively, on the total loads, 15.5 × 10^9 tons solids/yr and 37,400 km^3 water/yr.
Sources: After Martin and Meybeck 1979; Martin and Whitfield 1981; Meybeck 1979, 1982.

Berner and Berner, "Global Environment"

Climate dependency

- T affects rate of dissolution, elemental solubility and secondary mineral stability

- T and H_2O affects the local biology (biomass and type)
  - Riverine TOC increases as biomass increases
  - Type affects depth of physical weathering by roots, burrows, etc..

Climate dependency example:
Weathering of the same silicate rock will create in a watershed:

tropical climate: much higher suspended load proportions of Al and Fe to other elements due to more intense rock weathering and incongruent dissolution.

temperate climate: much greater relative amounts of Ca, Mg, K, Na to Al and Fe in s-load because weathering is less “intense”

Rock Types Effect on Riverine TDS:

sedimentary rock > volcanic rock > crystalline rock *(intrusive and metamorphic)*

Note: Chemical Denudation Rate is a measure of TDS flux per unit time out of a watershed. Greater runoff and high TDS both increase overall transport.

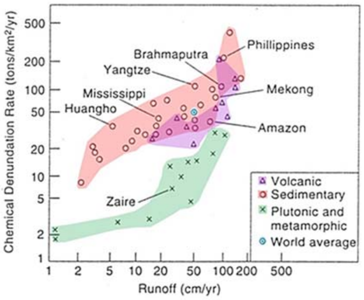


Figure 5.7. Influence of rock composition on total dissolved load per unit area (chemical denudation rate) versus runoff per unit area for major world rivers and some small basins. Certain major rivers discussed in the text are also included. (Adapted from Meybeck 1980; additional data from Hu et al. 1982.)

Berner and Berner, "Global Environment"

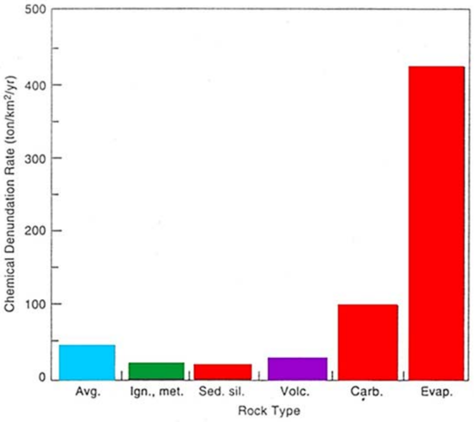


Figure 5.8. Relative chemical denudation rate in tons/km²/yr of various rock types compared to the average rate. Abbreviations for rock types are as follows: avg. = average; ign., met. = igneous and metamorphic; sed. sil. = sedimentary silicates; volc. = volcanics; carb. = carbonates; evap. = evaporites. (Data from Meybeck 1987.)

We see **rock type** and **climate** effects together in dissolved SiO_2, which in most natural waters is *essentially all is from silicate rocks*.

Dissolution rate depends on temperature and rock type. Temperature dependence involves 2 factors. As T increases :

- dissolution rate increases
- biological production of dissolved organic acids increases

Dissolved silica is highest in waters of tropical volcanic terrains such as Hawaii

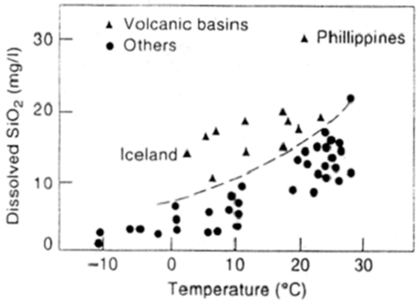


Figure 5.6. Variation in dissolved silica content of world rivers (mg/l SiO_2), with average temperature of drainage basin (°C) for nonvolcanic and volcanic basins. (After Meybeck 1980.)