

(Schlesinger & Bernhardt: Chapter 8)

## **River transport and chemistry**

### **Lecture Outline**

1. Introduction – Overview
2. Soil Hydraulics & Stream Hydrology
3. Stream Load
  - a) Biogeochemical Transformations of C, N, and P
  - b) Other Dissolved Constituents
  - c) Suspended Load
4. Summary

# Introduction - Overview

- Rivers are more than conduits from land to sea: important biogeochemical reactions occur **within** rivers.
  - Ch 4: stream water chemistry: a metric of weathering rates
  - Ch 6: stream water records nutrient loss from terrestrial ecosystems
- In-river transformations of organic C, N, P
- We will also examine:
  - factors that control the flow of stream waters
  - constituents in stream water and their origin

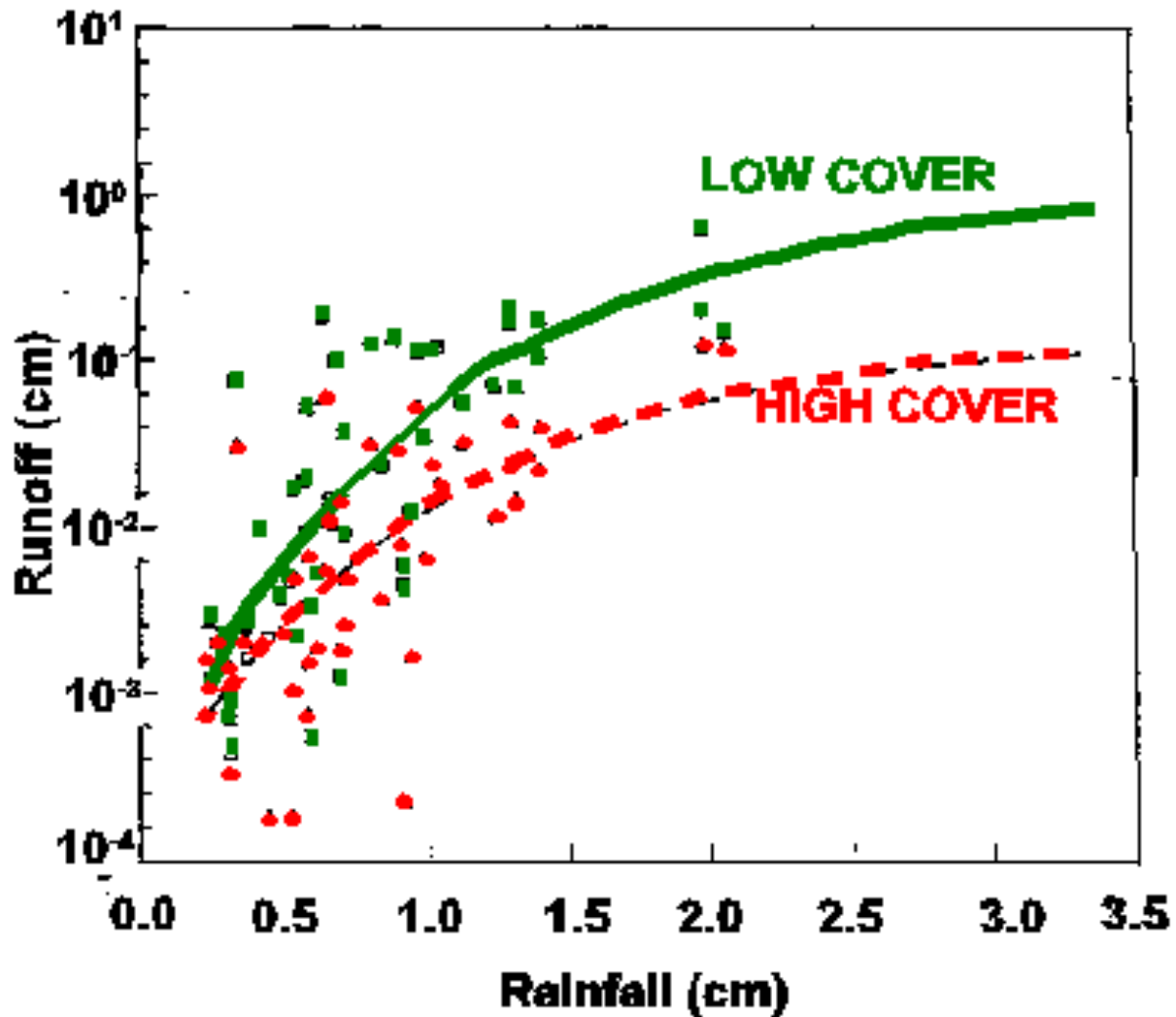
# Soil Hydraulics & Stream Hydrology

## (Water flow through soils)

- Rivers result from the runoff of water from the continents
- Precipitation, the ultimate source of river water,
  - Can be evaporated from the land
  - Can pass to shallow depths in the soil (surface flow)
  - Can pass to greater depths and remain in the ground over longer time scales (groundwater)

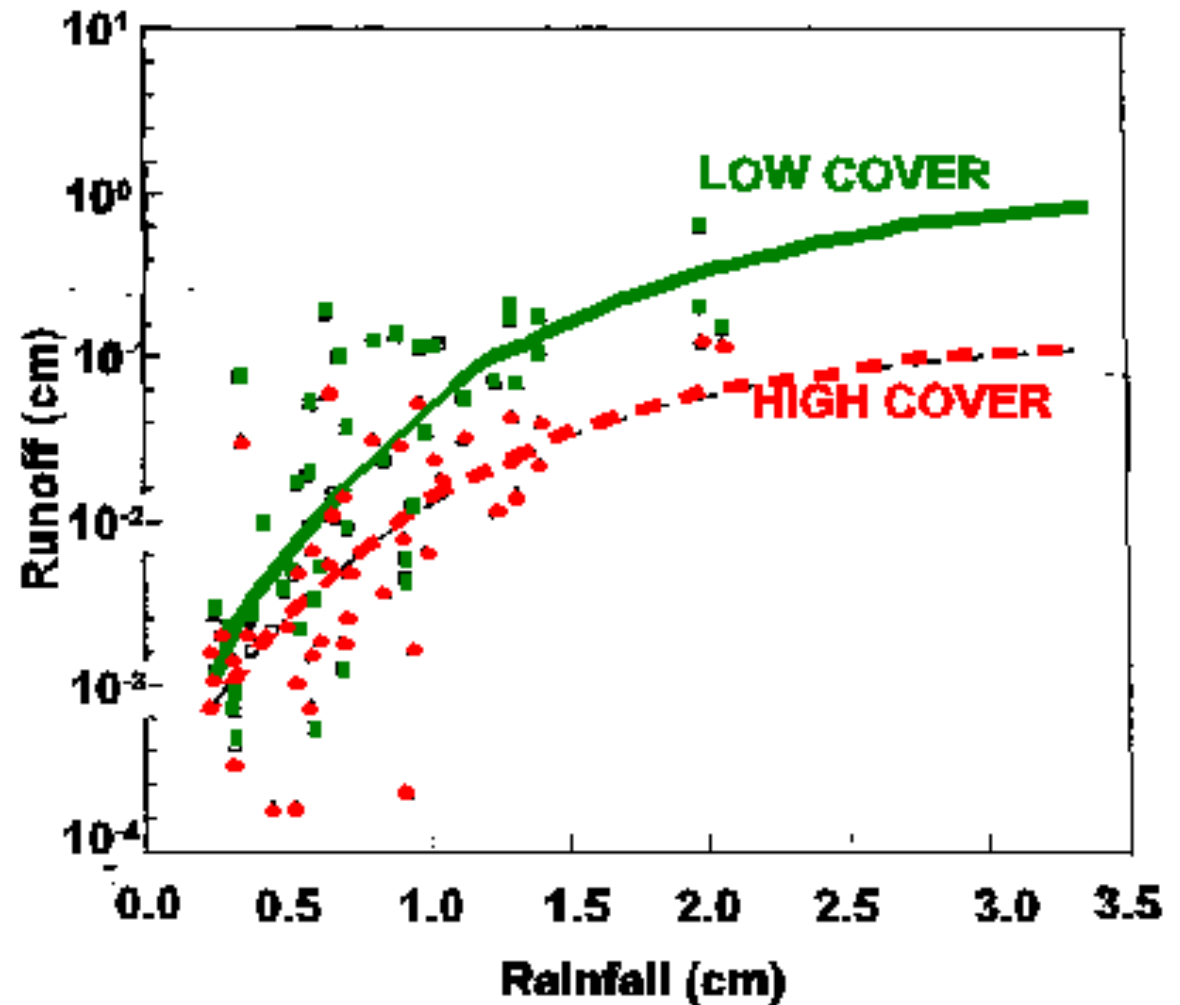
## Figure for Class Discussion

Data are from 2 grassland plots, with different amounts of grassland coverage



# Runoff from high- and low-grassland plots as a function of rainfall (Fig. 8.1, 2<sup>nd</sup> ed.)

- Runoff is low when rainfall is low.
- Runoff increases as rainfall increases.
- Runoff decreases as vegetation cover increases.



# Vegetation Impacts Soil Holding Capacity

- Reduces runoff:
  - Lowers initial impact energy of raindrops, reducing soil erosion and allowing greater time for soil infiltration
  - Plant roots, earthworms, other soil organisms promote downward percolation of moisture through soil pores
  - Increases surface roughness, slowing the runoff rate relative to bare soils
- Reduces average soil moisture content:
  - plant root uptake of soil water
- When vegetation is removed, soil water content and runoff increase

# Evaporation and Plant Transpiration reduce soil moisture and runoff

Table reports % of growing season precipitation

VEGETATION	% Evaporation	% Transpiration	% Runoff, Recharge
Tropical Rainforest	18	48	34
Temperate Forest	13	32	55
Temperate Grassland	35	65	0
Steppe	55	40	5
Desert	28	72	0

(condensed from Table 8.1, 2<sup>nd</sup> ed.)

- Runoff from wet forests can be substantial.
- Dry systems (steppe, desert) have little to no runoff.
- Transpiration (biotically induced water loss) typically exceeds evaporation (meteorological water loss).

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# Soil Porosity and Texture affect Runoff

- Soil properties (porosity, texture) affect infiltration rates and soil water content.

Soil Pore Volume = Porosity

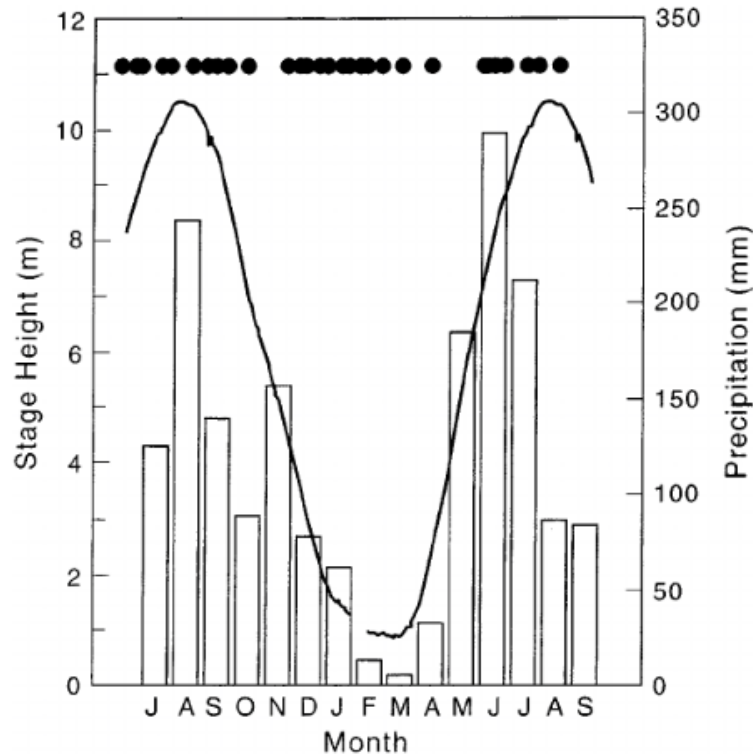
= total void space per volume sediment

- Sands (> 2 mm) have higher porosity than clays (< 0.002 mm)
  - Water infiltrates sands more rapidly than clay-dominated soils
  - As soils dry, clays retain higher water content than coarser soils

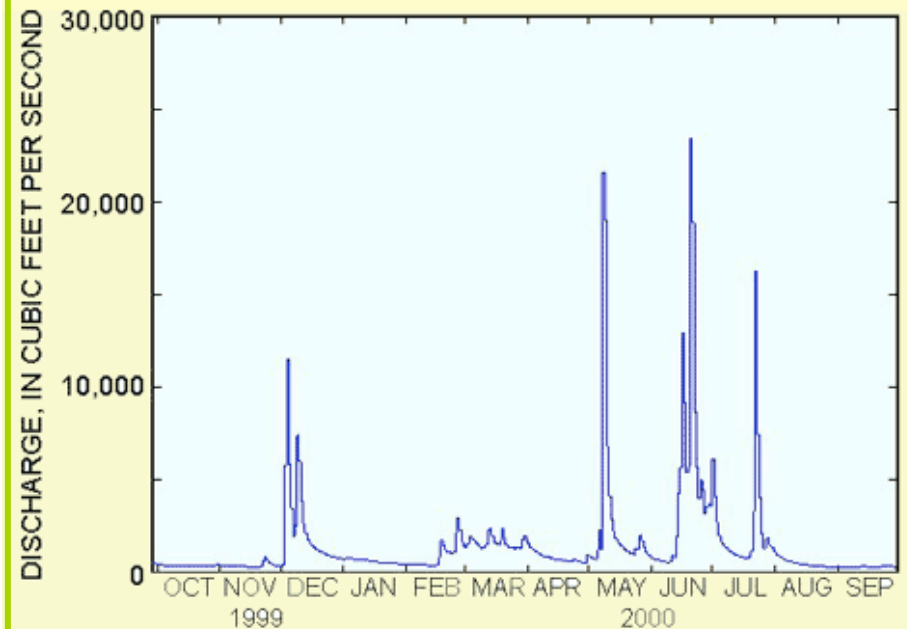
# Field Capacity and Flow: Definitions

- When percolation of water  $>$  soils water holding capacity and plant uptake rate, downward water flow occurs.
- Water-holding ability = “**field capacity**”
  - The water content a soil can hold against the force of gravity.
- Field capacity is a function of:
  - porosity (high in sands, low in clays)
  - water retention (low in sands, high in clays)
  - presence of impermeable layers
- When excess water drains to the base of the soil profile, it drains into a stream channel
- Groundwater height  $\approx$  stream height
- During the dry season (no precipitation) stream flow is maintained by the slow drainage of the soil ( = “**base flow**”)

# Stream Hydrographs: Flow vs. Time

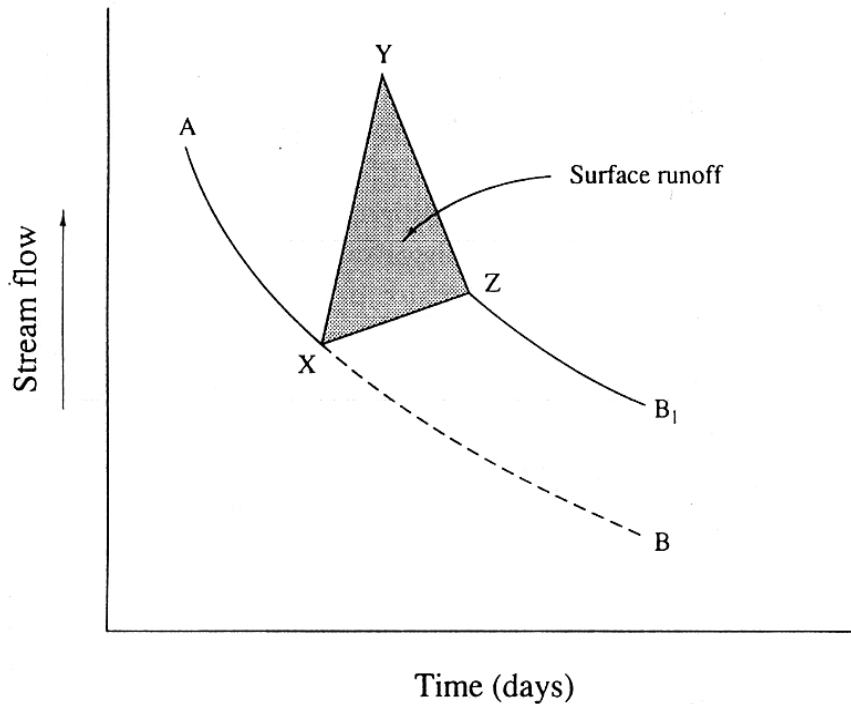


Lower Orinoco River, which has a large drainage basin and extensive flood plain, has a **smoothly varying annual hydrograph** (solid line); precipitation (bars). Filled circles indicate sampling dates (1991 and 1992). (Smith et al. (2000). Biogeochemistry. 51.



He'eia Stream has a **"Flashy" hydrograph**. Rivers in mountainous areas with small drainage basins exhibit spikes in flow immediately after rainfall events, and a rapid return to pre-storm flow rates. ([www.carleton.edu](http://www.carleton.edu))

# Storm Impact on Stream Hydrographs



**Figure 8.2** A stream hydrograph, showing the effect of a rainstorm at time *X* on stream runoff, which increases to a peak (*Y*) during the rainstorm. Streamflow declines rapidly to base flow (*Z*), which is reestablished at a higher level (*B<sub>1</sub>*) than if the storm had not occurred (*B*). Modified from Ward (1967).

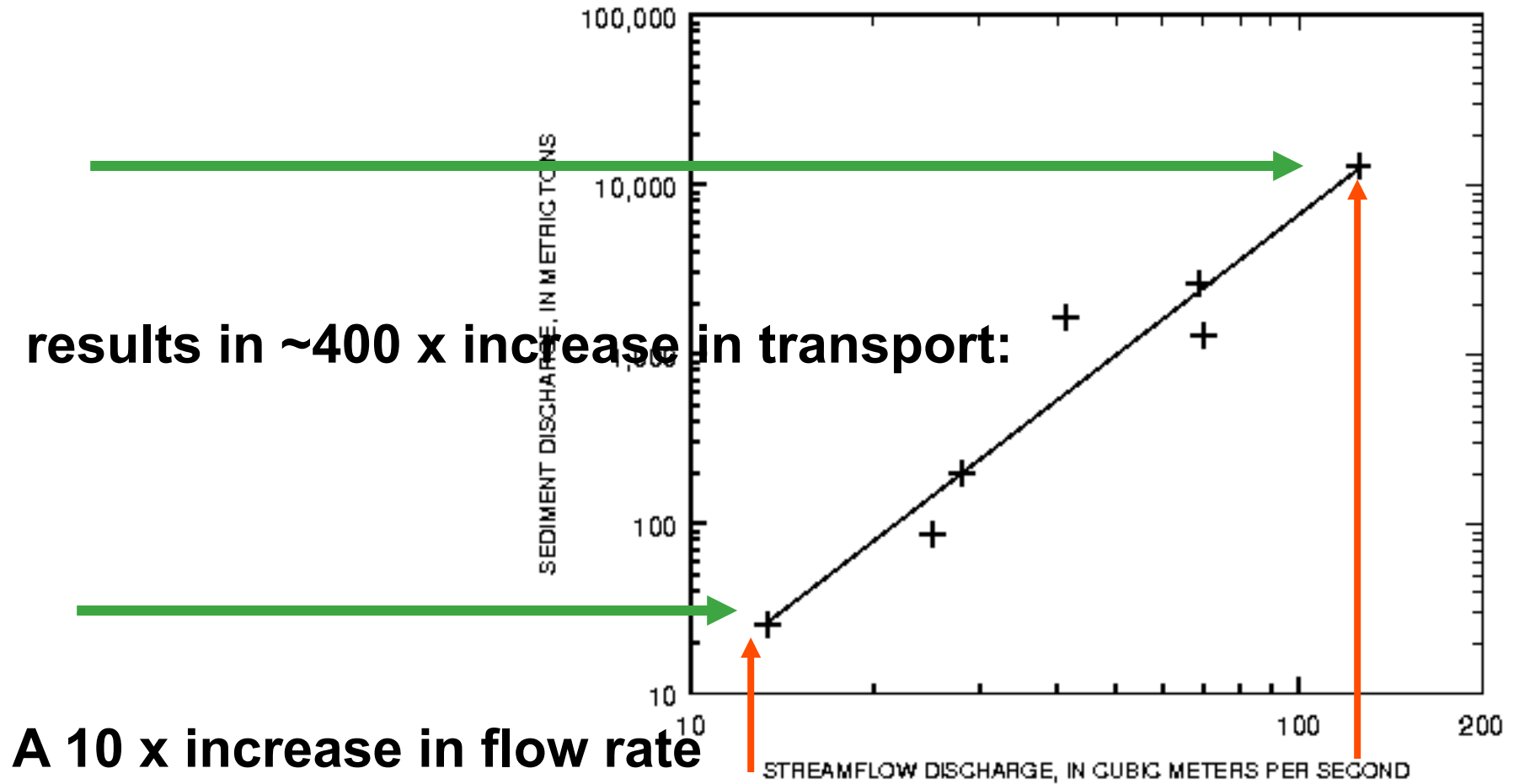
Schlesinger (200x), 2<sup>nd</sup> edition

- Base flow declines slowly as drought continues.
- Stream flow increases immediately with precipitation due to surface runoff.
- Post-storm, surface runoff ceases, but elevated soil moisture content increases the amount available for drainage.
- Stream hydrograph shows the fraction of flow derived from surface runoff vs. drainage of soil water.
- Surface runoff may carry organic debris and soil particles.
- In tropical rainforests, base flow can be 92% of total flow; in deserts storm flow dominates, rivers are turbid.

# Stream Load

- River components:
  - Water
  - Dissolved material (total dissolved solids (*TDS*))
    - major species:  $\text{HCO}_3^-$ ,  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$
  - Particulate matter
    - major elements: Al, Fe, Si, Ca, K, Mg, Na, P
- *TDS* derived from rainfall and soil solution after it has interacted with soil particles (exchange reactions) and bedrock (chemical weathering)
- Particulate matter derives from mechanical weathering: represents erosion and transport from soil surface.
  - Includes suspended load and bed load
  - Size ranges from colloidal clays to boulders, leaves to logs

# Suspended flux is function of flow rate



# Nutrient and carbon sources

- Small streams: Allochthonous POC and DOC > Autochthonous
- Larger, slowly moving rivers: Autochthonous sources > Allochthonous sources
  - Production of OM that is more labile than terrestrial OM
  - Labile OM can fuel complex food webs
  - Respired DOC and POC lost to atmosphere as CO<sub>2</sub>
  - Ratio of DOC:POC increases in large rivers; they have a smaller 'edge' effect
- DOC and POC usually increase with stream flow, due to greater contribution of surface flow
- The river continuum concept - Ecosystem productivity increases with stream size. In general:
  - Narrow, shaded headwaters, terrestrial OM inputs dominate, R>P
  - As channels widen, benthic algae and macrophytes increase
  - Larger rivers, allochthonous OM dominates (again) as waters are too fast & turbid to support primary producers, P>R

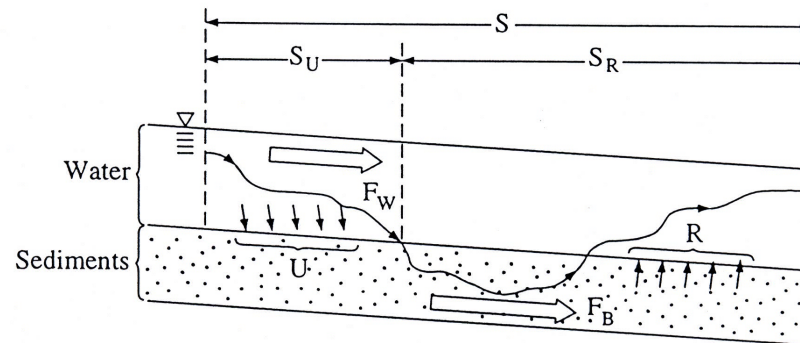


# Riverine Macronutrients: N & P

- Most rivers carry low concentrations of DIN ( $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ) and DIP ( $\text{HPO}_4^{2-}$ ), which are actively taken up by plants and soil microbes and retained on land (Chap. 6).
- Autochthonous production in streams is nutrient limited; shifts from net heterotrophy to autotrophy can occur with the addition of P.
- Decomposition rates are limited by substrate quality, and can increase with P-additions.
- Decomposition of POC results in decreased C:N and C:P, similar to what is seen during decomposition of terrestrial litter, and is due to P and N immobilization by microbes, and P-sorption.
- A significant fraction of N and P is carried in particulate matter (organic and inorganic) and as dissolved organic nutrients; inorganic forms are less abundant. Seasonal inundation of floodplains provide a source of N & P from deposited sediments that can stimulate NPP.

# Nutrient Spiral: A Nutrient Cycle Displaced by Advective Flow

- N&P is retained in rivers by biological (N & P) and abiotic (mostly P) pathways
- Nutrient recycling: microbial respiration returns N&P to bioavailable forms that can be taken up by primary producers
- Multiple respiration-uptake cycles during transport increases N&P residence times
- Cycle occurs most rapidly when biotic activity is highest; the 'spiral length' ( $S$ ) is inversely related to ecosystem metabolism.



**Figure 8.4** Nutrient spiraling in a two-compartment stream. Spiraling length,  $S$ , is the sum of the uptake length,  $S_U$ , and the remineralization length,  $S_R$ .  $F_w$  is the downstream flux of dissolved nutrients in the water compartment and  $F_b$  is the downward flux in the particulate compartment. Modified from Newbold et al. (1982).

# Riverine Macronutrients: Anthropogenic Effects

- Global N & P riverine transport has increased due to fertilizers and phosphate detergent usage.
- Meybeck (1982) estimates N is 2x and P is 3x pre-industrial levels
- Increase not globally uniform, but concentrated in population centers
- Ban on P-detergent has lowered P-loading; N-loading has continued to increase.
- Reduction of P lowers NPP, OM content in sediments, anaerobic respiration -> reducing transport of soluble reduced toxic metals (e.g. Cd).

Table 8.4 Recent Changes in the Delivery of Nitrogen and Phosphorus in Rivers to Coastal Areas of the United States<sup>a</sup>

Region	Change in load, 1974–1981	
	Total nitrate (%)	Total phosphorus (%)
Northeast Atlantic coast	32	–20
Long Island Sound/New York Bight	26	–1
Chesapeake Bay	29	–0.5
Southeast Atlantic coast	20	12
Albemarle/Pamlico Sound	28	0
Gulf Coast	46	55
Great Lakes	36	–7
Pacific Northwest	6	34
California	–5	–5

<sup>a</sup> From Smith et al. (1987). Copyright 1987 by the AAAS.

# Historical Trend of nitrate flux in the Mississippi River

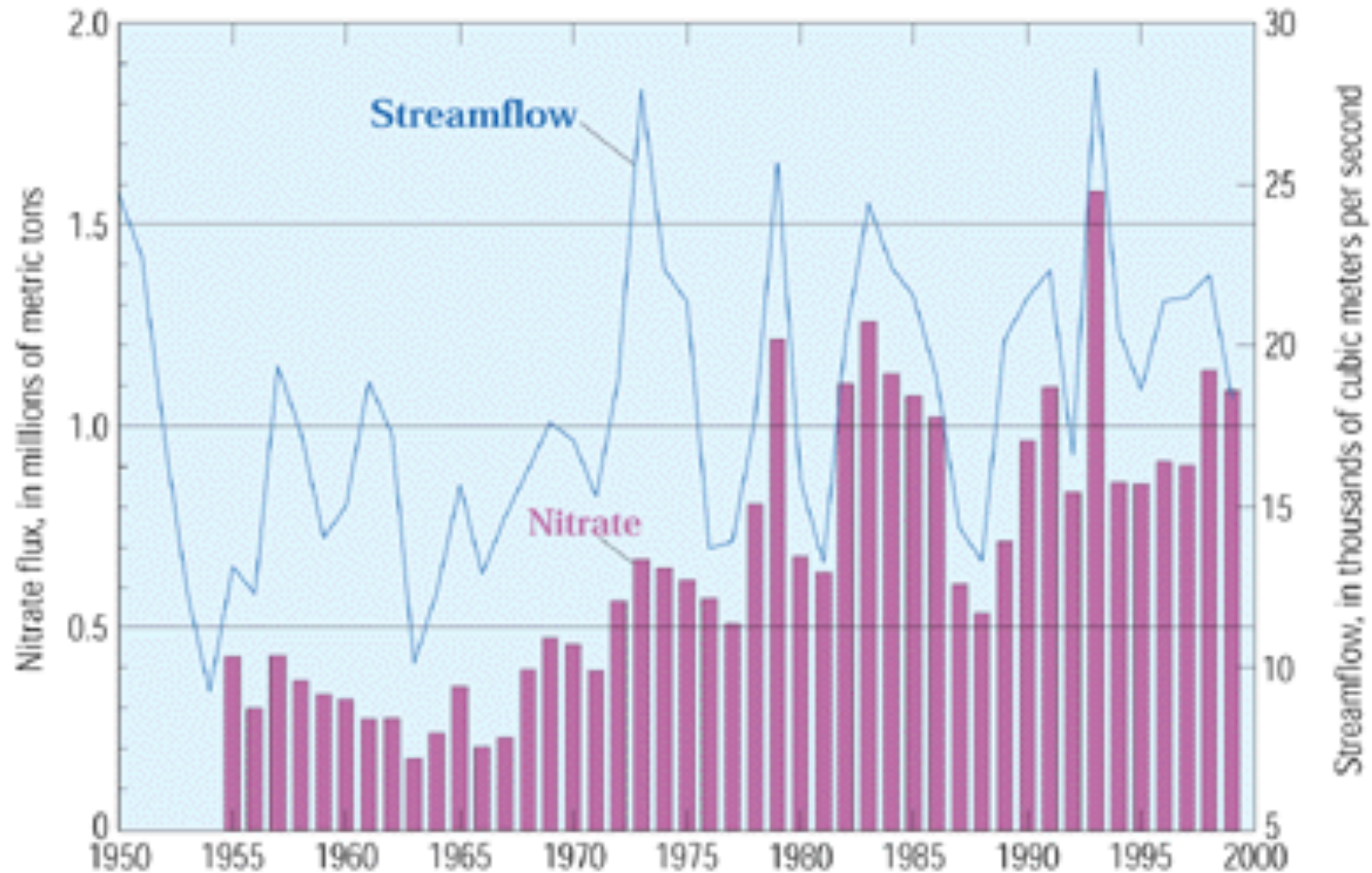


Figure 4. Annual nitrate flux and mean annual streamflow from the Mississippi River Basin to the Gulf of Mexico.

# Mississippi River drainage basin



Figure 1. Mississippi River drainage basin, major tributaries, and areal extent of 1999 midsummer hypoxic zone.

# Relationship of NO<sub>3</sub> flux to hypoxia in the Gulf of Mexico

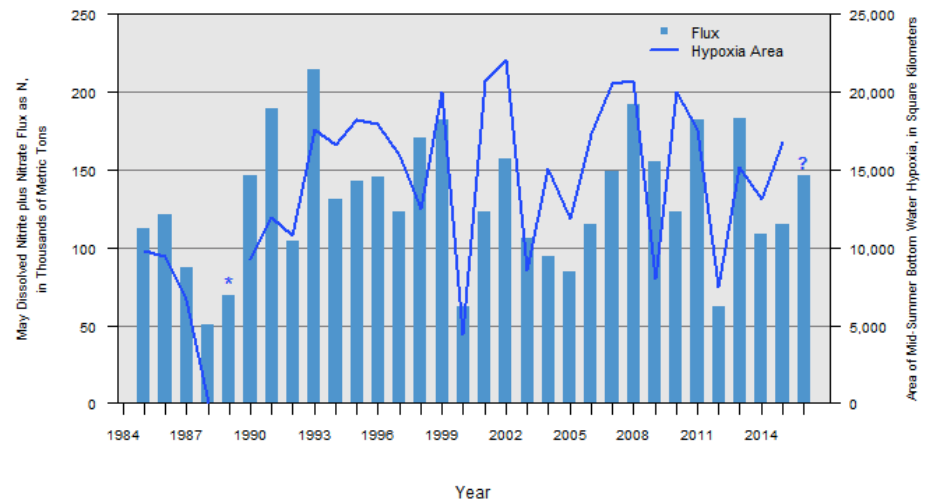
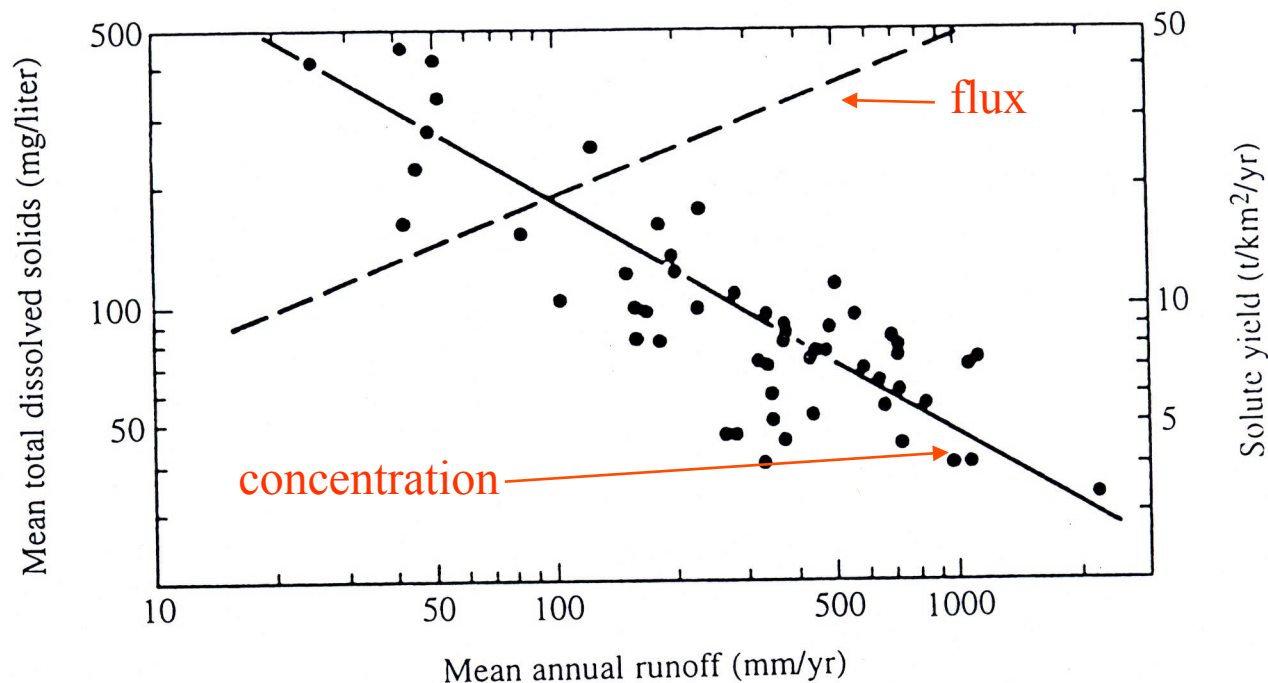


Figure 2. May dissolved nitrite plus nitrate flux to the Gulf of Mexico and area of mid-summer bottom water hypoxia (dissolved oxygen concentrations of less than 2 milligrams per liter) in the northern Gulf of Mexico. Data for 2016 are estimated using discrete water-quality samples and in-situ nitrate sensor data (previous years are estimated using discrete water-quality samples and daily streamflow data). Hypoxia area data from Nancy N. Rabalais, Louisiana Universities Marine Consortium. \*No hypoxia area data for 1989.

## Other Dissolved Constituents

- TDS concentration is related to discharge rate and origin of waters.
  - highest during low flow, because most water derives from soil profile, where it is in equilibrium with rock weathering and exchange reactions (chap. 4).
  - TDS declines with increasing flow due to dilution by water derived from precipitation and surface flow, with minimal contact with soil and bedrock.



**Figure 8.6** Variation of the concentration of total dissolved solids (solid line) and the total annual transport of dissolved substances (dashed line) for various streams in Kenya, as a function of mean annual runoff. From Dunne and Leopold (1978).

# Effects of high flow episodes

- TDS concentrations are often higher during rising limb of a hydrograph than during the declining limb
  - Initial flushing of concentrated soil waters that accumulate during low flow periods
- Sediment transport during occasional extreme events often exceeds total transport during long periods of normal flow
- Patterns are not consistent, so it is necessary to measure concentrations under *all* flow conditions and to integrate over long periods of time.

# Sources of major elements in World River Water

(Table 8.6, Schlesinger, 2<sup>nd</sup> ed).

Element	Atmospheric cyclic salt	Weathering			
		Carbonates	Silicates	Evaporites	Pollution
Ca <sup>2+</sup>	0.1	65	18	8	9
HCO <sub>3</sub> <sup>-</sup>	≤1	61	37	0	2
Na <sup>+</sup>	8	0	22	42	28
Cl <sup>-</sup>	13	0	0	57	30
SO <sub>4</sub> <sup>2-b</sup>	2	0	0	22	43
Mg <sup>2+</sup>	2	36	54	≤1	8
K <sup>+</sup>	1	0	87	5	7
H <sub>4</sub> SiO <sub>4</sub>	≤1	0	99+	0	0

- Nearly all Ca, Mg, K is derived from rock weathering
- Carbonate weathering is dominant source of Ca; silicates dominate Mg & K
- Na, Cl, SO<sub>4</sub> is derived mainly from marine aerosols (Chap. 3)
- Na > Cl due to weathering of Na-minerals
- Individual streams may vary from global averages, depending upon local conditions and terranes -> geology exerts a strong influence (carbonates, evaporites, etc.)
- Anthropogenic activity has increased NO<sub>3</sub> and SO<sub>4</sub>.
- 2/3 of bicarbonate in rivers is derived from atmosphere -> carbonic acid weathering



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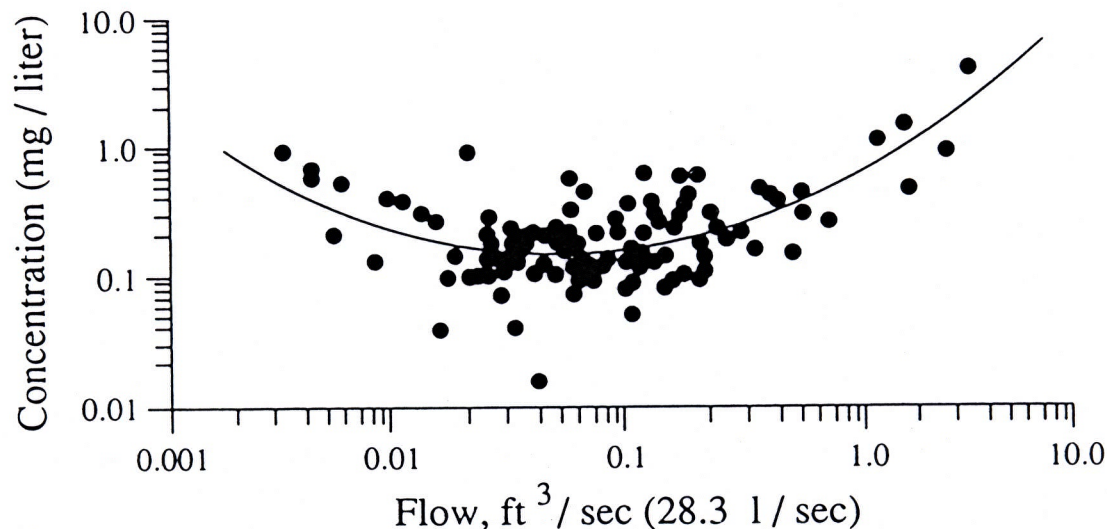
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# Suspended Load

- Suspended sediments are the products of mechanical weathering and erosion.
- Curvilinear trend results from high organic matter at low flow, decreasing as suspended sediment levels increase at higher flow, at highest flows erosion is greatest, leading to highest suspended sediment levels.
- Sediment transport during extreme events often exceeds total transport during long periods of more normal conditions (e.g. flash floods).



**Figure 8.8** Concentration of particulate matter as a function of stream flow in the Hubbard Brook Experimental Forest of New Hampshire. From Bormann et al. (1974).

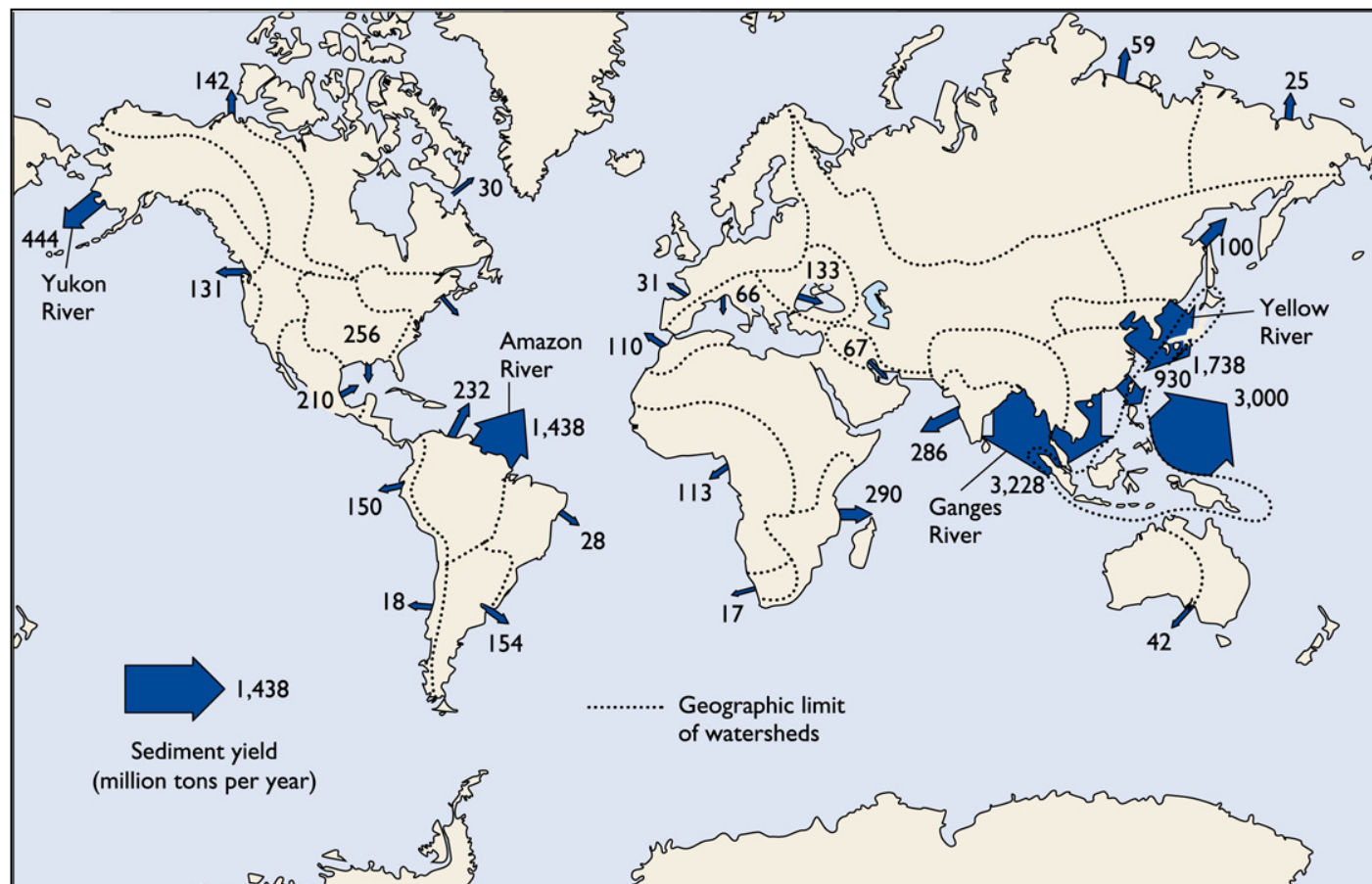
# Comparison of Dissolved and Suspended fluxes

Element	Dissolved Flux	Particulate Flux	Part:Diss
	$10^6$ t/yr	$10^6$ t/yr	
Al	2	1457	729
Ca	501	333	0.7
Fe	1.5	744	496
K	49	310	6
Mg	125	183	1.5
Na	193	110	0.6
Si	181	4418	24
P	1	18	18

**Considerable variation among chemical species**

# Global Riverine Sediment Input to the Ocean

- Sediment discharge rate is not the same as total rate of soil erosion.
- Major controlling factors: elevation, topographic relief, climate (rainfall)
- Asia ( $\approx 30\%$ ), and Pacific and Indian Ocean Islands ( $\approx 45\%$ ) dominate sediment input, even though they do not rank as highest water discharge rivers, due to high sediment yield, or erodability of drainage areas.



# Lecture Summary

- Stream ecosystems are linked to biogeochemical reactions in surrounding terrestrial systems.
- Flow and chemical properties of stream water are determined by soil properties & vegetation in the watershed.
- Magnitude of stream water flow is controlled by:
  - vegetation
  - soil characteristics
- Most streams are heterotrophic, oxidizing more organic material than is produced in them, supersaturated w.r.t.  $\text{CO}_2$ . During stream transport, available forms of N and P are removed and sequestered in organic and inorganic forms.
- Streams carry other ions in both dissolved and particulate form, largely reflecting rock weathering.
- Humans have dramatically affected streams and rivers world-wide.
- Most sediment transport to the ocean is from Asia, Pacific and Indian ocean islands, due to climate, tectonics, and erodability.