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 just conduits from land to sea: important biogeochemical reactions occur within rivers.
  - Chap. 4: stream water chemistry as a metric of weathering rates
  - Chap. 6: stream water records nutrient loss from terrestrial ecosystems

- Our emphasis: 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
• River water ultimately comes from precipitation:
  – Can either 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 much longer (groundwater)
• Magnitude of stream water flow is controlled by:
  - vegetation
  - soil characteristics
Runoff from high- and low-grassland plots as a function of rainfall (Fig. 8.1, 2nd ed.)

- Runoff is low when rainfall is low.
- Runoff increases as rainfall increases.
- Runoff decreases as vegetation cover increases.
Effect of Vegetation on Holding Capacity of Soil

• Vegetation 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

• Vegetation may reduce average soil moisture content:
  - plant root uptake of soil
  - when vegetation is removed, soil water content and runoff increase
Plant transpiration reduces soil moisture and runoff (% of growing season precipitation)

(condensed from Table 8.1, 2nd ed.)

<table>
<thead>
<tr>
<th>VEGETATION</th>
<th>% Evaporation</th>
<th>% Transpiration</th>
<th>% Runoff, Recharge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tropical Rainforest</td>
<td>18</td>
<td>48</td>
<td>34</td>
</tr>
<tr>
<td>Temperate Forest</td>
<td>13</td>
<td>32</td>
<td>55</td>
</tr>
<tr>
<td>Temperate Grassland</td>
<td>35</td>
<td>65</td>
<td>0</td>
</tr>
<tr>
<td>Steppe</td>
<td>55</td>
<td>40</td>
<td>5</td>
</tr>
<tr>
<td>Desert</td>
<td>28</td>
<td>72</td>
<td>0</td>
</tr>
</tbody>
</table>

- 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).
Effect of Soil Texture and Porosity on Runoff

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

  \[
  \text{Soil Pore Volume} = \text{Porosity} = \text{total void space per volume sediment}
  \]

- Sands (> 2 mm) have a 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

- Downward water flow is assumed to occur when percolation of water exceeds soils water holding capacity and the rate of plant uptake.

- Water-holding ability of a soil is called its **field capacity**, or 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 bottom of the soil profile, it is assumed to be delivered to a stream channel

- Groundwater height $\approx$ stream height

- When precipitation is not occurring, stream flow is maintained by the slow drainage of the soil (**base flow**)
Stream Hydrographs: relate stream flow to time.

- Base flow declines slowly as drought continues.
- With precipitation, stream flow may increase immediately due to surface runoff.
- After the storm, surface runoff disappears, but soil moisture content has increased, increasing 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.

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 (B₁) than if the storm had not occurred (B). Modified from Ward (1967).
Stream Load

• River water can be thought of as being made up of a number of 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 include: $\text{Al}$, $\text{Fe}$, $\text{Si}$, $\text{Ca}$, $\text{K}$, $\text{Mg}$, $\text{Na}$, $\text{P}$)

• **TDS** is largely derived from rainfall and from soil solution after it has interacted with soil particles (exchange reactions) and bedrock (chemical weathering)

• Particulate matter derives from mechanical weathering, and represents erosion and transport from soil surface.
  – Includes suspended load and bed load
  – Includes material ranging from colloidal clays to boulders, leaves to logs
Suspended flux is function of flow rate

A 10 x increase in flow rate results in ~400 x increase in transport:
Nutrient and carbon sources

- Allochthonous POC and DOC > autochthonous in smaller streams
- In contrast, autochthonous sources > in larger, more slowly moving rivers
  - 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$_2$
  - Ratio of DOC:POC increases in large rivers; they have a smaller ‘edge’ effect, and DOC, CPOM is degraded in-river
- 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.
Estimating global riverine C transport

*problems of scaling in biogeochemistry*

• **Approach #1:**
  – Study land-to-stream transfer of C in many types of small watersheds
  – Multiply transfer from each type of watershed by the global area occupied by each watershed type
  – Emphasizes loss of OC from land

• **Approach #2:**
  – Study large rivers and plot C load at river mouth vs. annual river flow
  – Use regression to
    • Estimate C load in rivers not studied
    • Estimate global C load from all rivers
  – Emphasizes transfer of OC to ocean
Approach #2: Use large rivers and measure annual flow and OC load near river mouth.

- Largest rivers are critical to this approach, since 50 of the largest rivers carry 43% of the total freshwater to the ocean.
- The Amazon alone carries 20%.
- The difference between Approaches #1 and #2 will be due to the OC metabolized during transport, deposited in flood plains or behind dams.

**Figure 8.3** Total annual load of organic carbon shown as a logarithmic function of total annual riverflow for major rivers of the world. Rivers 1–7 are among the 50 largest: 1, Amazon; 2, Mississippi; 3, St. Lawrence; 4, MacKenzie; 5, Danube; 6, Volga; and 7, Rhine. From Schlesinger and Melack (1981), with a revision of the data for the St. Lawrence derived from Pocklington and Tan (1987).
Riverine Macronutrients: N & P

- Most rivers carry low concentrations of DIN (NH$_4^+$, NO$_3^-$) and DIP (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, and shifts from net heterotrophy to autotrophy can occur with the addition of P.

- Decomposition rates are also 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 Spiraling ≈ Recycling

- 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.

*Spiral vs. closed cycle because recycling occurs in moving water*

Ex.: P flows downstream @ 10.4 m/d, cycling 1x every 18.4 d; average spiral length is 190 m. (determined using $^{15}$N & $^{32}$P)

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 greatly due to fertilizers and phosphate detergent usage.
- Meyeck (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>
<thead>
<tr>
<th>Region</th>
<th>Change in load, 1974–1981</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total nitrate (%)</td>
</tr>
<tr>
<td>Northeast Atlantic coast</td>
<td>32</td>
</tr>
<tr>
<td>Long Island Sound/New York Bight</td>
<td>26</td>
</tr>
<tr>
<td>Chesapeake Bay</td>
<td>29</td>
</tr>
<tr>
<td>Southeast Atlantic coast</td>
<td>20</td>
</tr>
<tr>
<td>Albemarle/Pamlico Sound</td>
<td>28</td>
</tr>
<tr>
<td>Gulf Coast</td>
<td>46</td>
</tr>
<tr>
<td>Great Lakes</td>
<td>36</td>
</tr>
<tr>
<td>Pacific Northwest</td>
<td>6</td>
</tr>
<tr>
<td>California</td>
<td>-5</td>
</tr>
</tbody>
</table>

*From Smith et al. (1987). Copyright 1987 by the AAAS.
Trend of nitrate flux in the Mississippi River

Figure 3.— Estimated annual flux of nitrate-N from the Mississippi River basin to the Gulf of Mexico — 1955–1998
Other Dissolved Constituents

- Concentration of TDS is related to discharge rate and to the origin of waters.
- TDS concentrations are 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 levels decline 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
  - This results from initial flushing of concentrated waters that accumulate in soil pores during low flow periods
- Sediment transport during occasional extreme events often exceeds the 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

Table 8.6 Sources of Major Elements in World River Water
(in Percent of Actual Concentrations)\(^a\)

<table>
<thead>
<tr>
<th>Element</th>
<th>Atmospheric cyclic salt</th>
<th>Weathering</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Carbonates</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>0.1</td>
<td>65</td>
</tr>
<tr>
<td>HCO(_3^-)</td>
<td>≪1</td>
<td>61</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>8</td>
<td>0</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>13</td>
<td>0</td>
</tr>
<tr>
<td>SO(_4^{2-})</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>2</td>
<td>36</td>
</tr>
<tr>
<td>K(^+)</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>H(_4)SiO(_4)</td>
<td>≪1</td>
<td>0</td>
</tr>
</tbody>
</table>

- Nearly all Ca, Mg, K is derived from rock weathering
- Carbonate weathering is dominant source of Ca; silicates dominate Mg & K
- Na, Cl, SO\(_4\) 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\(_3\) and SO\(_4\).
- 2/3 of bicarbonate in rivers is derived from atmosphere -> carbonic acid weathering
River composition as a function of water origin (Gibbs 1970).

Arid-climate (evaporative) rivers have even higher concentrations and are back to Cl dominance, bicarbonate is lost to mineral precipitation.

As weathering becomes important, proportion Cl goes down, TDS concentration goes up, bicarbonate dominates Cl.

River runoff dominated by precipitation is proportionally high in Cl (recycled salt) and low in total concentration.
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

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

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 (≈30%), and Pacific and Indian Ocean Islands (≈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 intimately tied to biogeochemical reactions in the surrounding terrestrial systems.

• Flow and chemical properties of stream water are determined by soil properties & vegetation in the watershed.

• Most stream systems are heterotrophic, oxidizing more organic material than is produced in them, supersaturated w.r.t. CO$_2$. During stream transport, available forms of N and P are removed and sequestered in organic an 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.