Solutes in the catchment hydrological system

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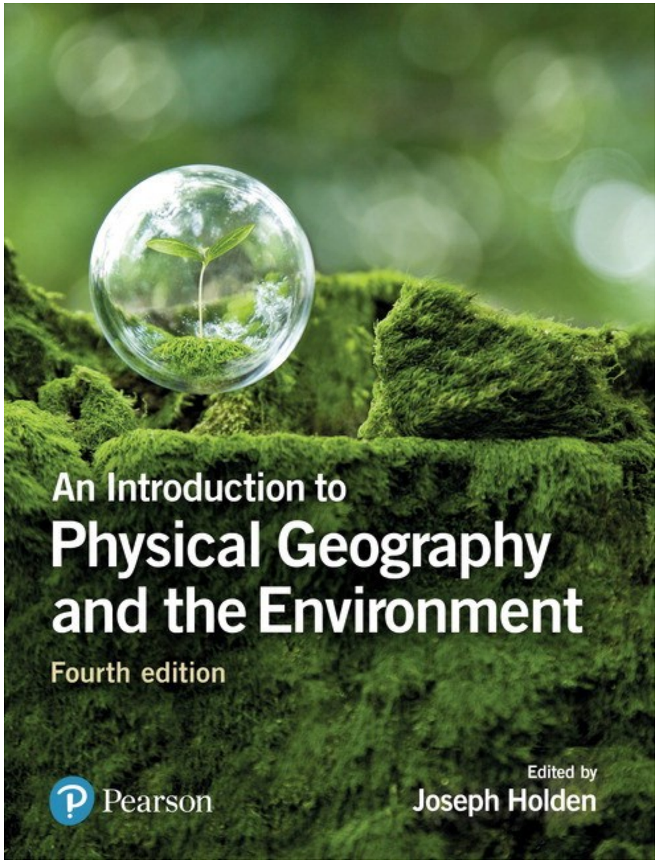


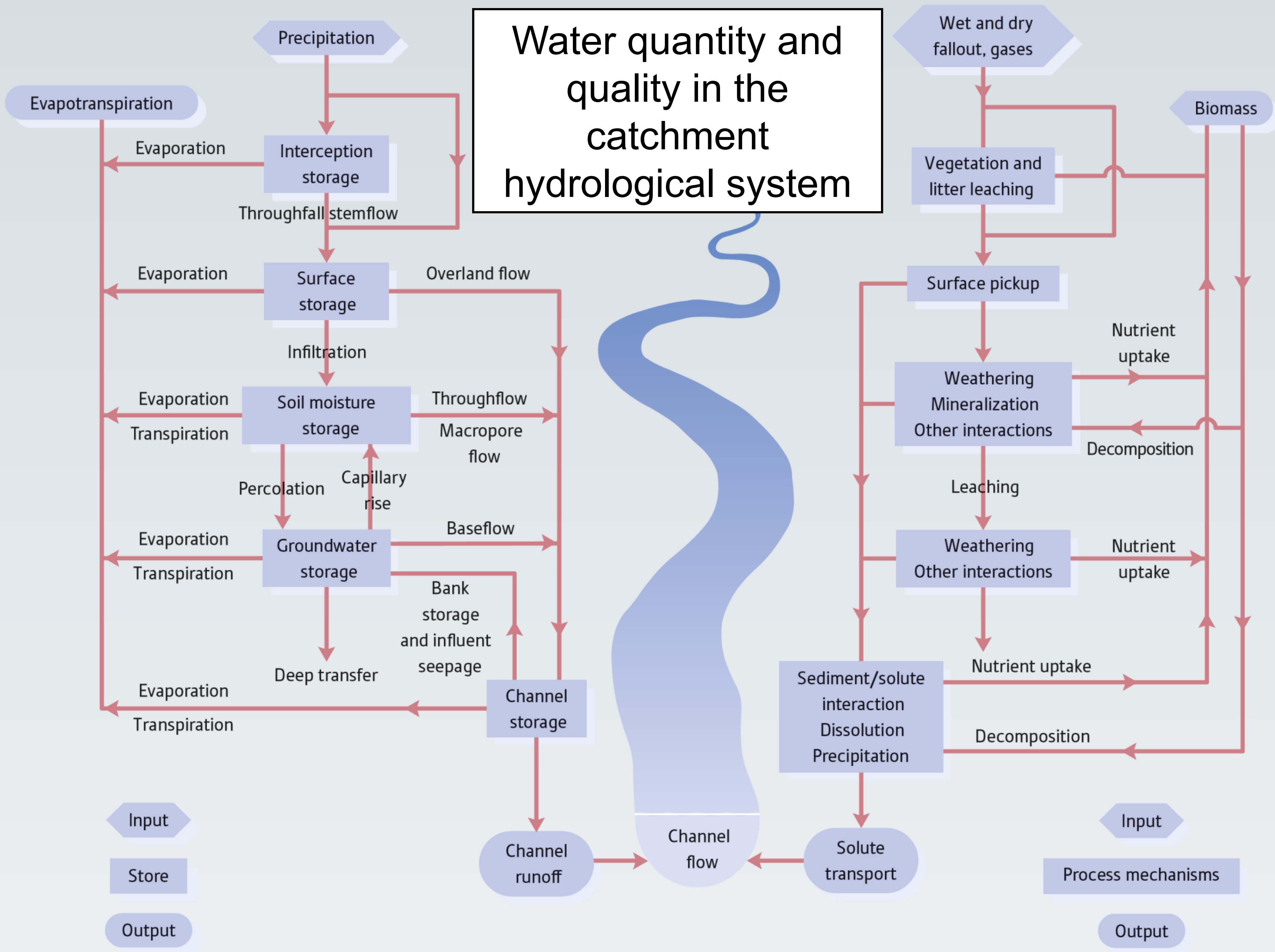
See Chapter 20 – *Online access via Library webpages*

Soil, Water & Atmospheric Processes

Solutes

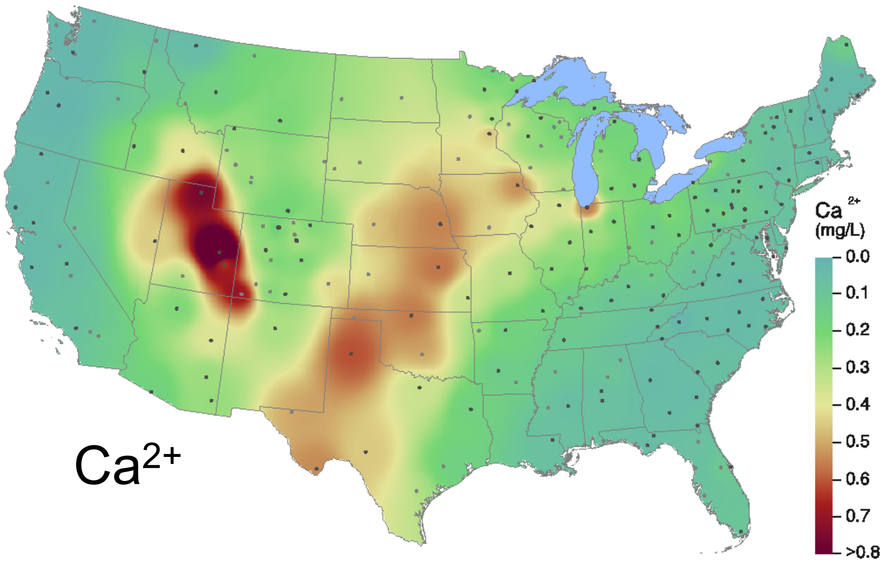
- Comprise metal ions, anions and organics in solution
- Why interested in solutes?
  - Water supply and public health
  - Industry and agriculture
  - Pollution control
  - Fisheries
  - Aquatic ecosystem health
  - Recreational use of water
  - Scientific research

Water quantity and quality in the catchment hydrological system



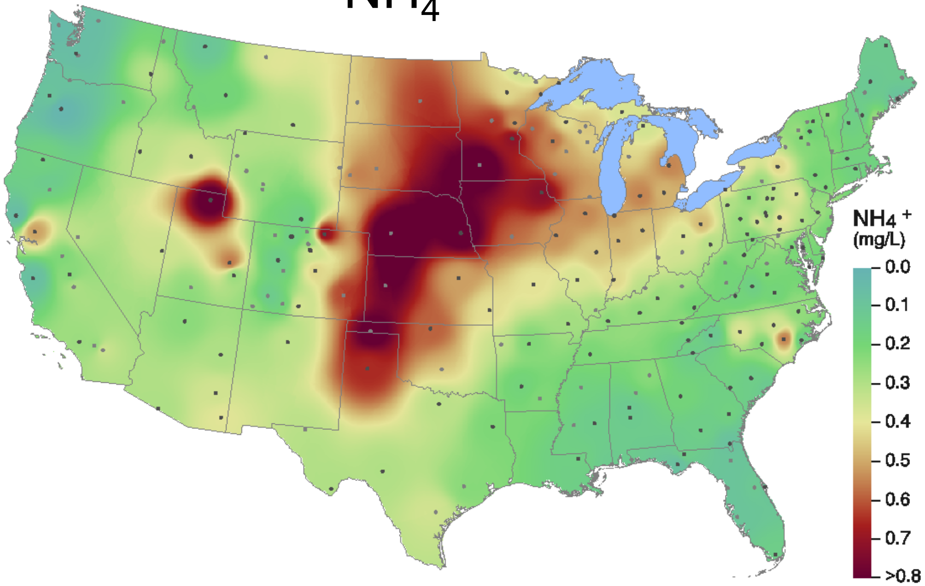
Factors affecting solute concentrations in precipitation

1. Marine salts
2. Wind-blown dust
3. Atmospheric pollution



Ca^{2+}

NH_4^+



Mean rainfall concentrations (mg L^{-1})
2012-14 Source: USEPA

WET and DRY deposition inputs

Atmospheric deposition	% from dry deposition in UK in 2006
Sulfur	20
Oxidised nitrogen (NO_2, NO_3^-, nitric acid)	52
Reduced nitrogen (NH_3, NH_4^+)	32

(RoTAP, 2012)

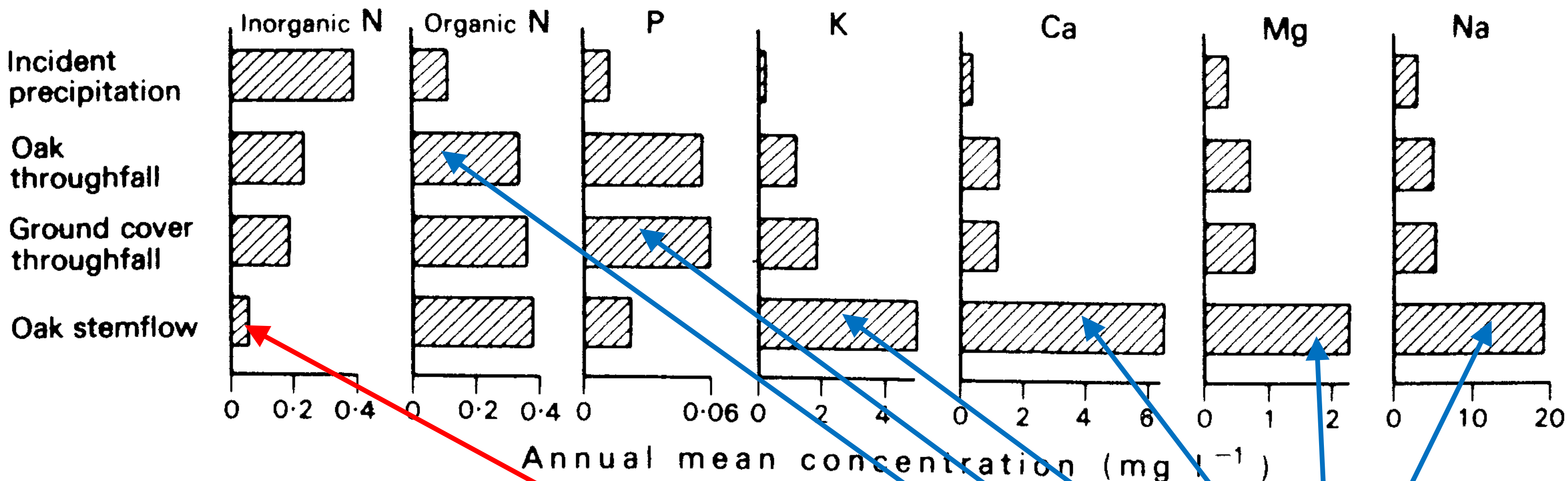
Evaporation => salt concentration

Devil's Golf Course, Death Valley, California

Salar de Uyuni, Bolivian altiplano

Interception by vegetation

Sessile oak woodland, Grizedale Forest, Lancashire, UK



Loss of solutes:
Uptake in canopy

Gain of solutes:

Washoff of dry deposition and plant exudates

Soil water reactions

1. <u>Cation exchange</u>

$$\underset{\text{(attached to colloid)}}{Ca^{2+}} + \underset{\text{(soil solution)}}{2H^{+}} \leftrightarrow \underset{\text{(attached to colloid)}}{2H^{+}} + \underset{\text{(soil solution)}}{Ca^{2+}}$$

2. <u>Anion adsorption</u> (e.g. SO_4^{2-}, PO_4^{3+})

3. <u>Mineral weathering</u>

4. <u>Decomposition</u>

   e.g. nitrification

   $NH_4^+ + 2O_2 \leftrightarrow NO_3^- + H_2O + 2H^+$

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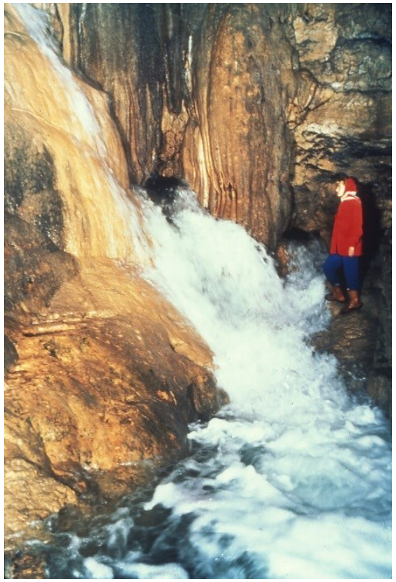
Groundwater

- High solute concentrations
- Variations in groundwater solute concentrations due to
  1. Residence time
  2. Geology



Rainwater has lower solute concentrations than groundwaters

Serpentinite groundwater has lower solute concentrations than other rock types as more resistant to weathering

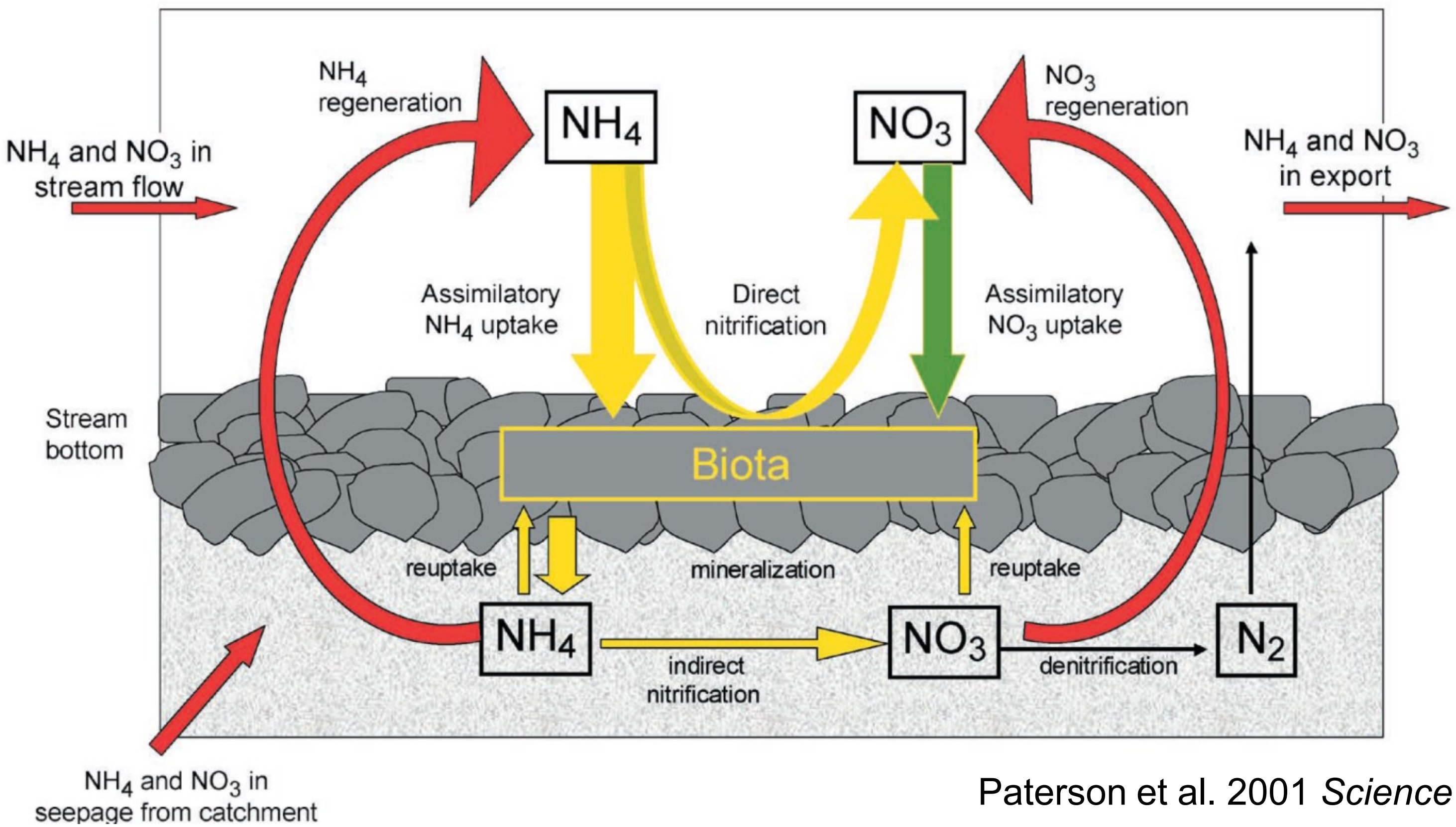
Parameter Units mg L^{-1}	Rainwater	Serpentinite	Limestone/ schist/ sandstone
Sodium	4.8	15.4	119
Calcium	0.8	5.2	457
Magnesium	4.5	44.7	50.9
Sulfate	< limit of detection	8.9	1300
Chloride	5.7	16.6	37.3
Total dis-solved solids	24	329	2210

(Fagundo-Castillo et al., 2008)

In-channel processes

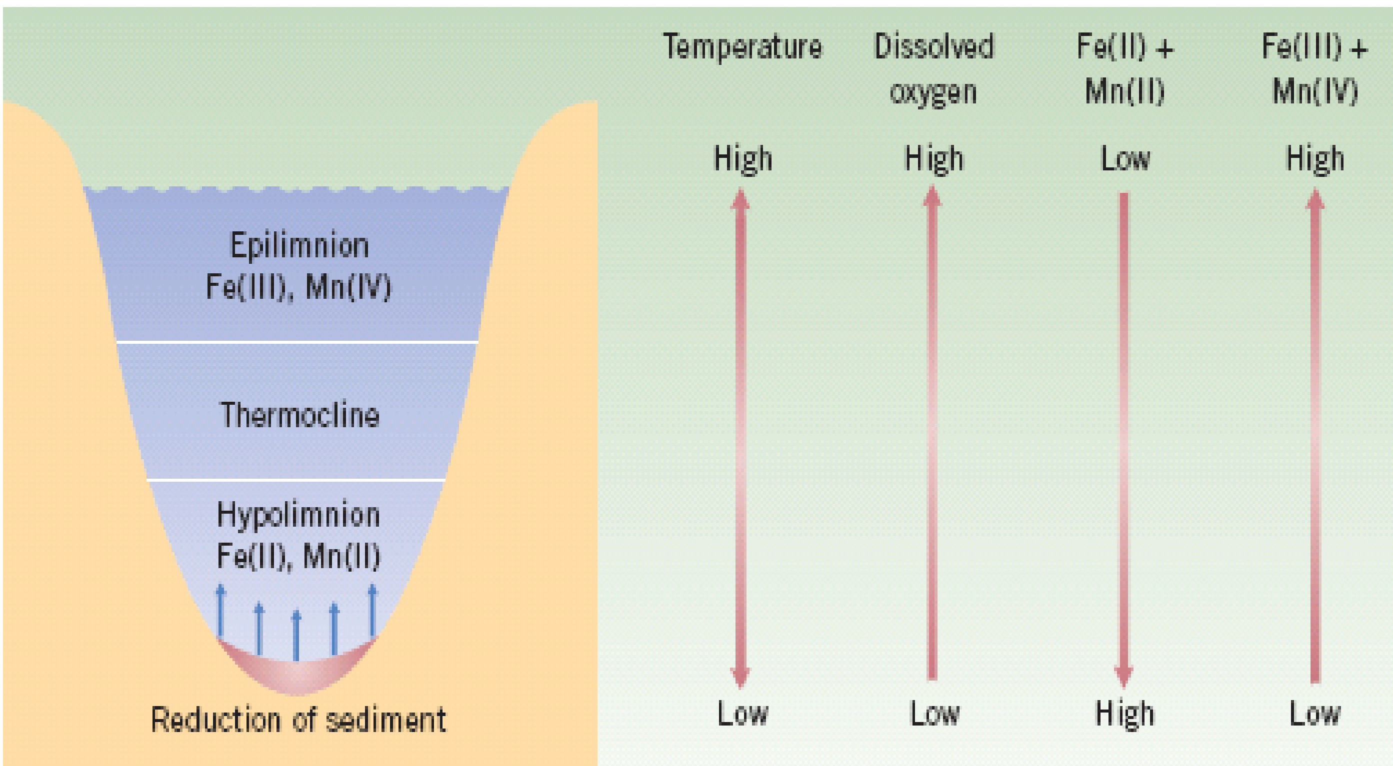
- Rapid cation exchange in pipe flow
- Adsorption and precipitation of metals and dissolved organic carbon on channel sediment
- Uptake of nutrients by vegetation and microbes in channel sediment

>50% of dissolved inorganic nitrogen input taken up in headwater streams in seasons of high biological activity (Paterson et al., 2001)

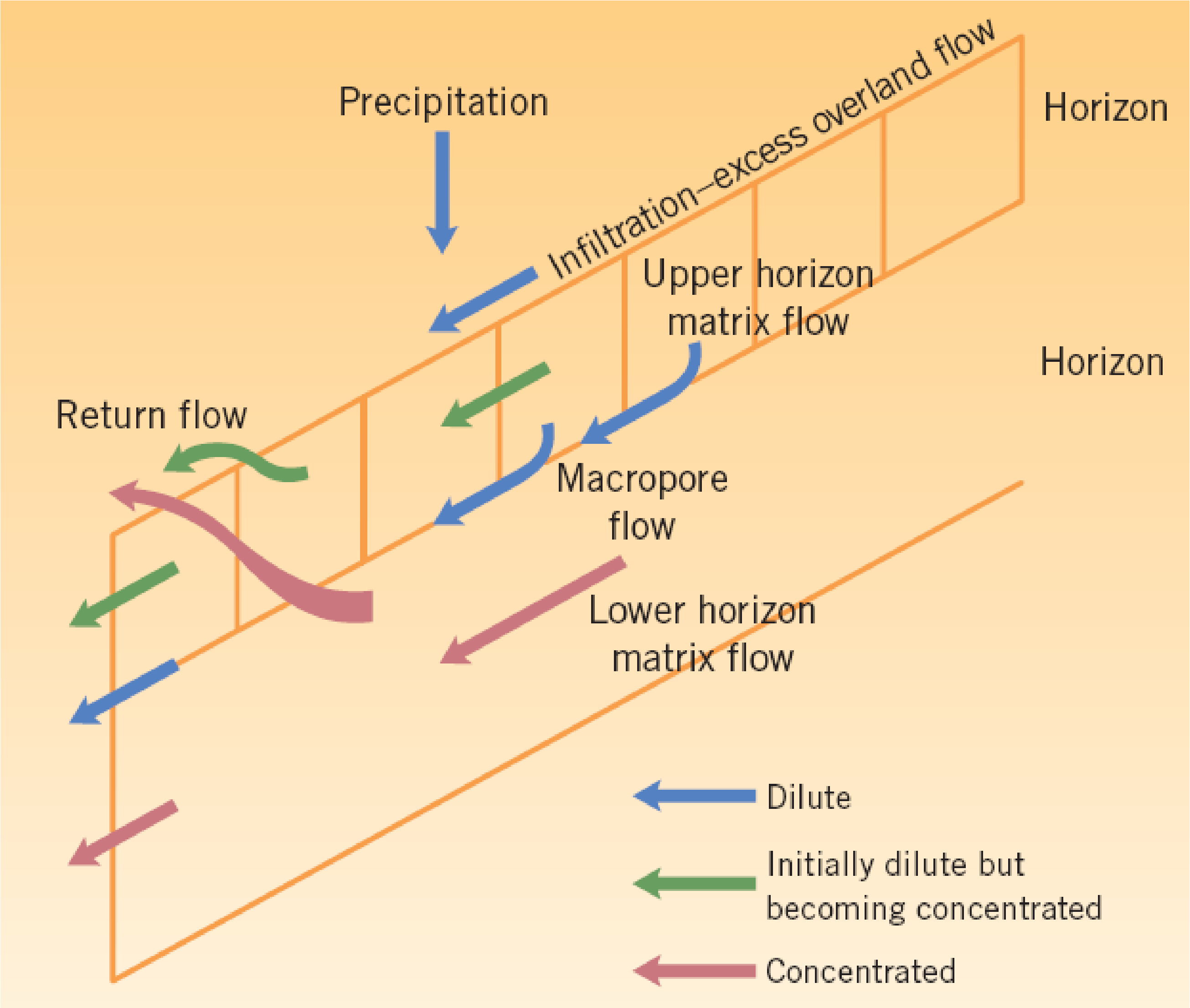


Paterson et al. 2001 *Science* **292**, 86-90

Biogeochemical cycling in lakes/reservoirs



Different contributions to streamflow have different solute characteristics => separation of storm hydrograph into runoff components

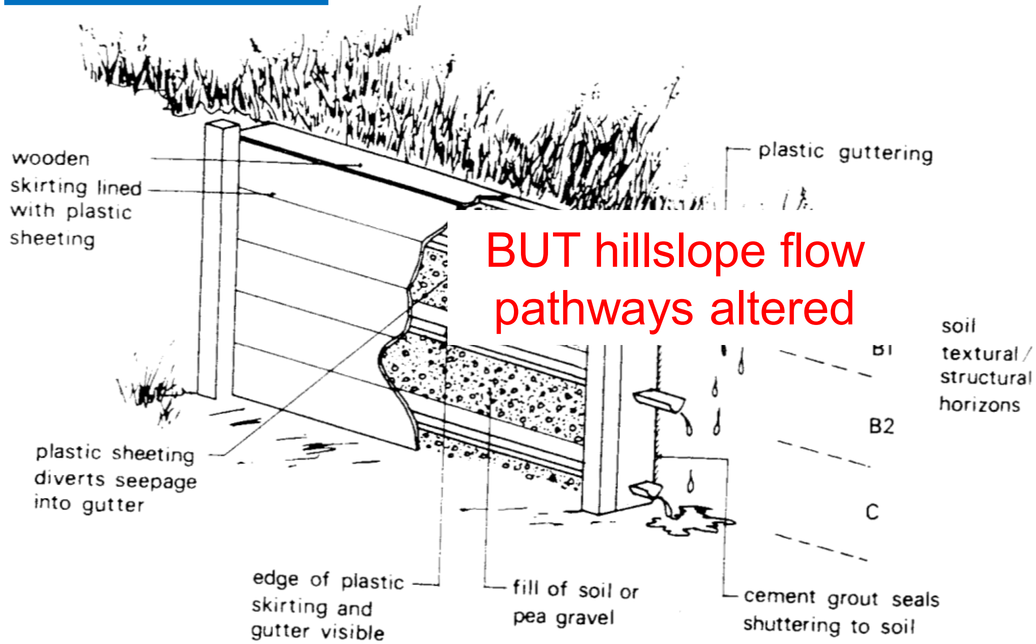


Sampling different water types

Groundwater:
sample from wells

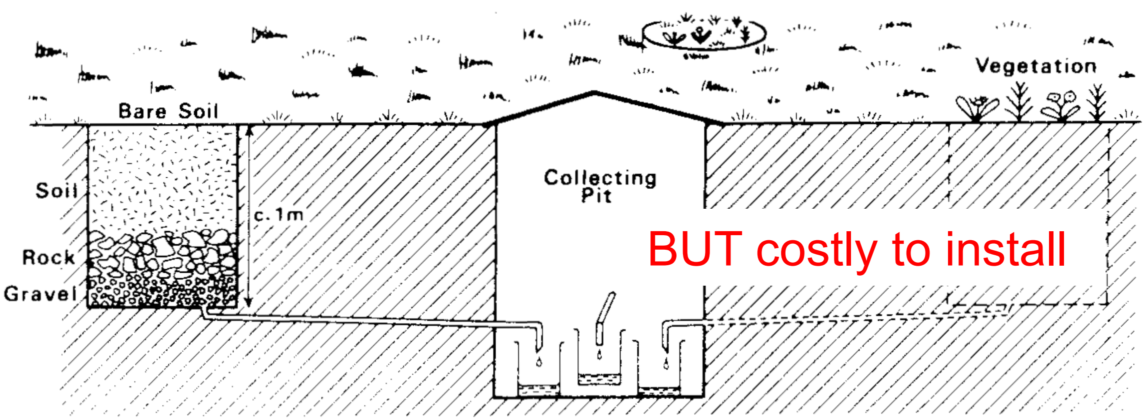
Soil water sampling

1. Gutters



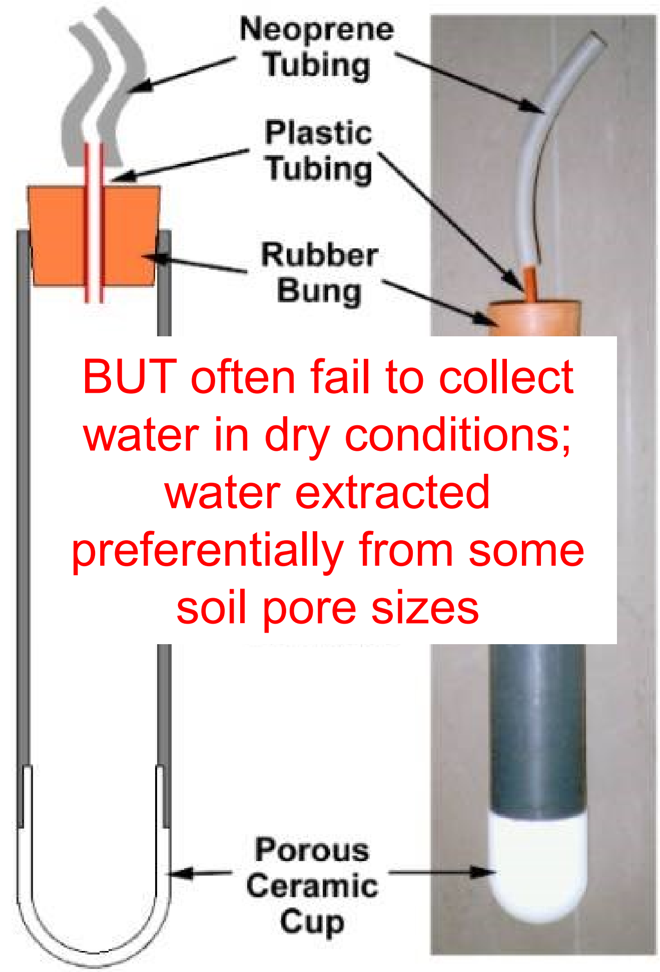
BUT hillslope flow pathways altered

2. Zero tension lysimeters



BUT costly to install

3. Suction cup samplers



BUT often fail to collect water in dry conditions; water extracted preferentially from some soil pore sizes

River water sampling

- "Grab" sample
- Automatic water samplers

- Well-mixed water
- Recommended sampling points and depths in rivers

Average Q ($m^3\ s^{-1}$)	*Type of river/stream*	*No sampling points*	*No sampling depths*
< 5	Small stream	2	1
5-140	Stream	4	2
150-1000	River	6	3
≥ 1000	Large river	≥ 6	4

(Bartram & Ballance, 1996)

Lake and reservoir waters

- No. sample sites = $\log_{10}$ lake area (in km^2)
  - e.g. lake of 100 km^2 area requires 2 sampling sites
- Need to take account of water quality variation with depth:
  - 1 m below water surface
  - just above thermocline
  - just below thermocline
  - 1 m above bottom sediment

General water sampling principles

- Appropriate sample container
- Sufficient water volume for analyses

Analysis	Sample volume (ml)	Analysis	Sample volume (ml)
Alkalinity	100	Kjeldahl nitrogen	400
Aluminium	25	Nitrate nitrogen	200
Biochemical oxygen demand	1000	Nitrite nitrogen	50
Boron	1	Phosphorus	100
Calcium	50	Potassium	100
Chloride	100	Selenium	1000
Fluoride	50	Silica	50
Iron	50	Sodium	100
Magnesium	75	Sulfate	200
Manganese	90	Total organic carbon	200
Ammonia nitrogen	400	Total suspended solids	1000

(Bartram & Ballance, 1996)

Variable	Recommended container[1]	Preservative	Max. permissible storage time
Alkalinity	Polyethylene	Cool 4 °C	24 h
Aluminium	Polyethylene	2 ml Conc. HNO_3 l^{-1} sample	6 months
Arsenic	Polyethylene	Cool 4 °C	6 months
BOD	Polyethylene	Cool 4 °C	4 h
Boron	Polyethylene	Cool 4 °C	6 months
Cadmium	Polyethylene	2 ml Conc. HNO_3 l^{-1} sample	6 months
Calcium	Polyethylene	Cool 4 °C	7 days
Carbamate pesticides	Glass	H_2SO_4 to pH < 4, 10g Na_2SO_4 l^{-1}	Extract immediately
Carbon			
inorganic/organic	Polyethylene	Cool 4 °C	24 h
particulate	Plastic Petri dish	Filter using GF/C filter; Cool, 4 °C	6 months
Chloride	Polyethylene	Cool 4 °C	7 days
Chlorinated hydrocarbon	Glass	Cool 4 °C	Extract immediately
Chlorophyll	Plastic Petri dish	Filter on GF/C filter; freeze –20 °C	7 days
Chromium	Polyethylene	2 ml Conc. HNO_3 l^{-1} sample	6 months
COD	Polyethylene	Cool 4 °C	24 h
Copper	Polyethylene	2 ml Conc. HNO_3 l^{-1} sample	6 months
Dissolved oxygen (Winkler)	Glass	Fix on site	6 h
Fluoride	Polyethylene	Cool 4 °C	7 days
Iron	Polyethylene	2 ml Conc. HNO_3 l^{-1} sample	6 months
Lead	Polyethylene	2 ml Conc. HNO_3 l^{-1} sample	6 months
Magnesium	Polyethylene	Cool 4 °C	7 days
Manganese	Polyethylene	2 ml Conc. HNO_3 l^{-1} sample	6 months
Mercury	Glass or teflon	1 ml Conc. H_2SO_4 + 1 ml 5% $K_2Cr_2O_7$	1 month
Nickel	Polyethylene	2 ml Conc. HNO_3 l^{-1} sample	6 months
Nitrogen			
Ammonia	Polyethylene	Cool 4 °C, 2 ml 40% H_2SO_4 l^{-1}	24 h
Kjeldahl	Polyethylene	Cool 4 °C	24 h
Nitrate + Nitrite	Polyethylene	Cool 4 °C	24 h
Organic nitrogen	Polyethylene	Cool 4 °C	24 h
Organic particulates	Plastic Petri dish	Filter using GF/C filter, Cool 4 °C	6 months
Organophosphorus pesticides	Glass	Cool, 4 °C, 10% HCl to pH 4.4	No holding, extraction on site
Pentachlorophenol	Glass	H_2SO_4 to pH < 4, 0.5 g $CuSO_4$ l^{-1} sample; Cool 4 °C	24 h
pH	Polyethylene	None	6 h
Phenolics	Glass	H_3PO_4 to pH < 4, 1.0 g $CuSO_4$ l^{-1} sample; Cool 4 °C	24 h
Phenoxy acid herbicides	Glass	Cool 4 °C	Extract immediately
Phosphorus			
Dissolved	Glass	Filter on site using 0.45 μm filter	24 h
Inorganic	Glass	Cool 4 °C	24 h
Total	Glass	Cool 4 °C	1 month

Variable	Recommended container[1]	Preservative	Max. permissible storage time
Potassium	Polyethylene	Cool, 4 °C	7 days
Residue	Polyethylene	Cool, 4 °C	7 days
Selenium	Polyethylene	1.5 ml Conc. HNO_3 l^{-1} sample	6 months
Silica	Polyethylene	Cool, 4 °C	7 days
Sodium	Polyethylene	Cool, 4 °C	7 days
Electrical conductivity	Polyethylene	Cool, 4 °C	24 h
Sulphate	Polyethylene	Cool, 4 °C	7 days
Zinc	Polyethylene	2 ml Conc. HNO_3 l^{-1} sample	6 months

[1] Teflon containers can also be used to replace either the polyethylene or glass containers shown in the table.

Source: Adapted from Environment Canada, 1981

(Bartram & Ballance, 1996)

Preservation and storage of water samples prior to analysis

Water sample analysis

Choice of parameters to measure depends on programme objectives

Field measurement

e.g. pH, dissolved O_2, conductivity

Laboratory analysis

Continuous flow analyser for nitrogen and phosphorus

Inductively coupled plasma mass spectrometer for trace elements