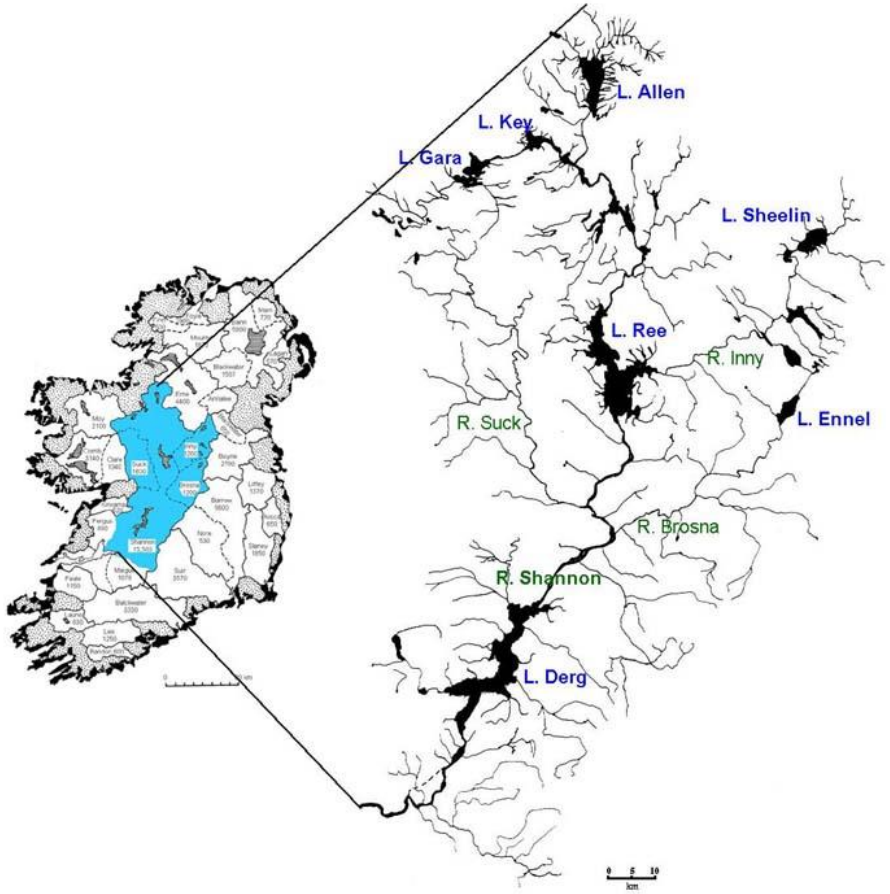
Limnology and Oceanography

Limnology: Catchment Geology and Water Chemistry Characteristics



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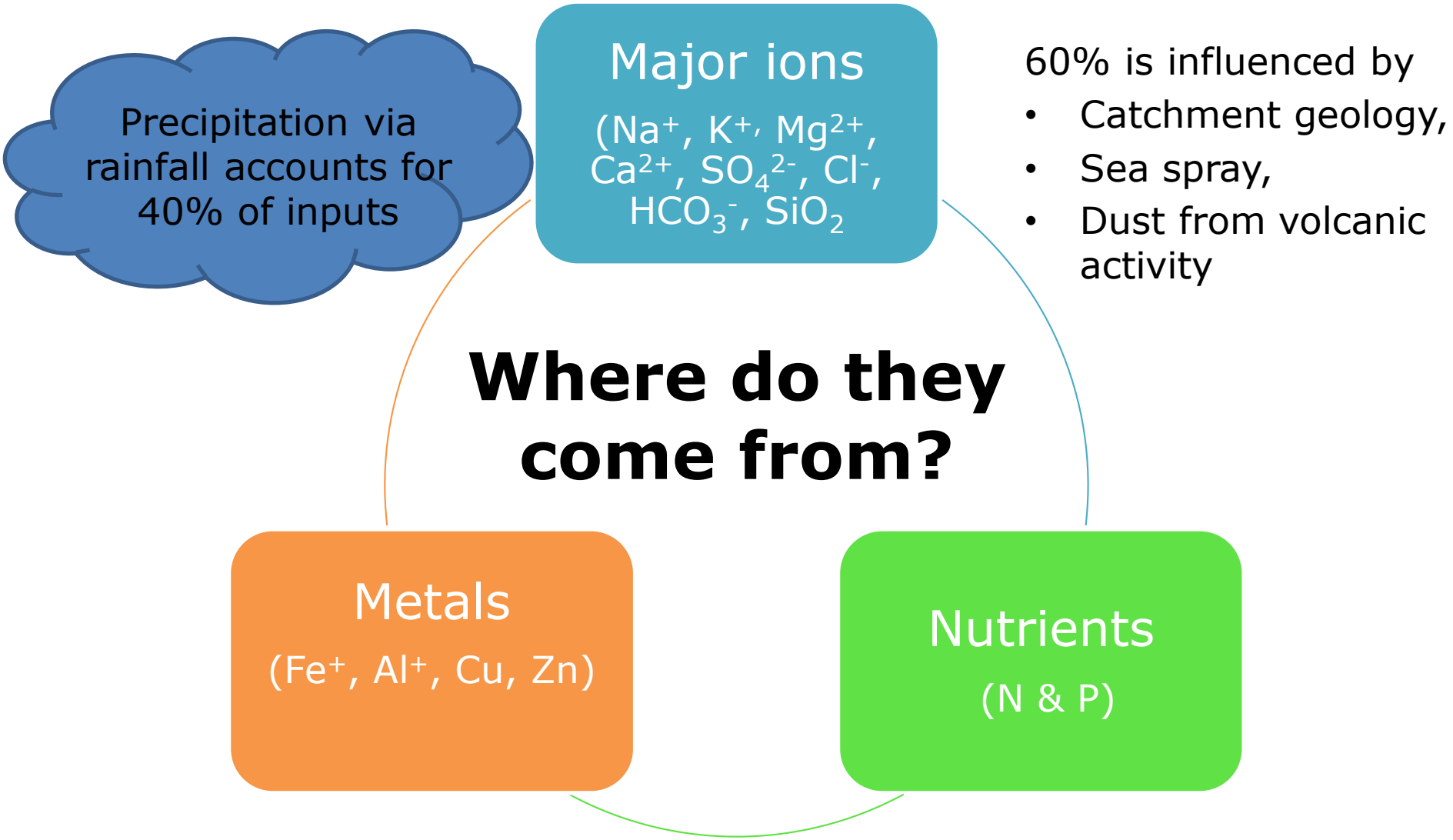
Learning Outcomes

To examine how catchment characteristics influence the chemical composition of freshwaters

To explore the key abiotic factors influenced by catchment characteristics and geology

How do catchment characteristics influence the chemical composition of freshwaters?

Chemical Composition of Freshwater



60% is influenced by

- Catchment geology,
- Sea spray,
- Dust from volcanic activity

Chemical Composition of Freshwater

mg/l	Rainfall (continental)	Rainfall (marine)	Rivers
Ca^{2+}	0.2 – 4.0	0.2 – 1.4	5.3 – 24.2
Mg^{2+}	0.05 - 0.5	0.4 – 1.5	1.4 – 5.2
Na^{+}	0.2 – 1.0	1.0 – 5.0	3.2 – 7.0
K^{+}	0.1 – 0.5	0.2 – 0.6	1.0 – 1.6
Cl^{-}	0.2 – 2.0	1.0 – 10	3.4 – 7.0
SO_4^{2-}	1.0 – 3.0	1.0 – 3.0	3.5 – 15.1
HCO_3-	0	0	26.7 – 80.1
SiO_2	0	0	6.8 – 16.3

Adapted from Allen (1995) after Berner and Berner (1987)

What Influences the Chemical Composition of Freshwater

Dissolved constituents vary with:

Type of Catchment

- Topography
- Geology
- Degree of catchment weathering
- Soils
- Vegetation
- Hydrology

Distance from Source

- Sources of water
- Conc. generally increase further from the headwaters

Discharge

- Depends on dissolved ion content, rainfall or industry & climate
- Mobility of ions in catchment soils

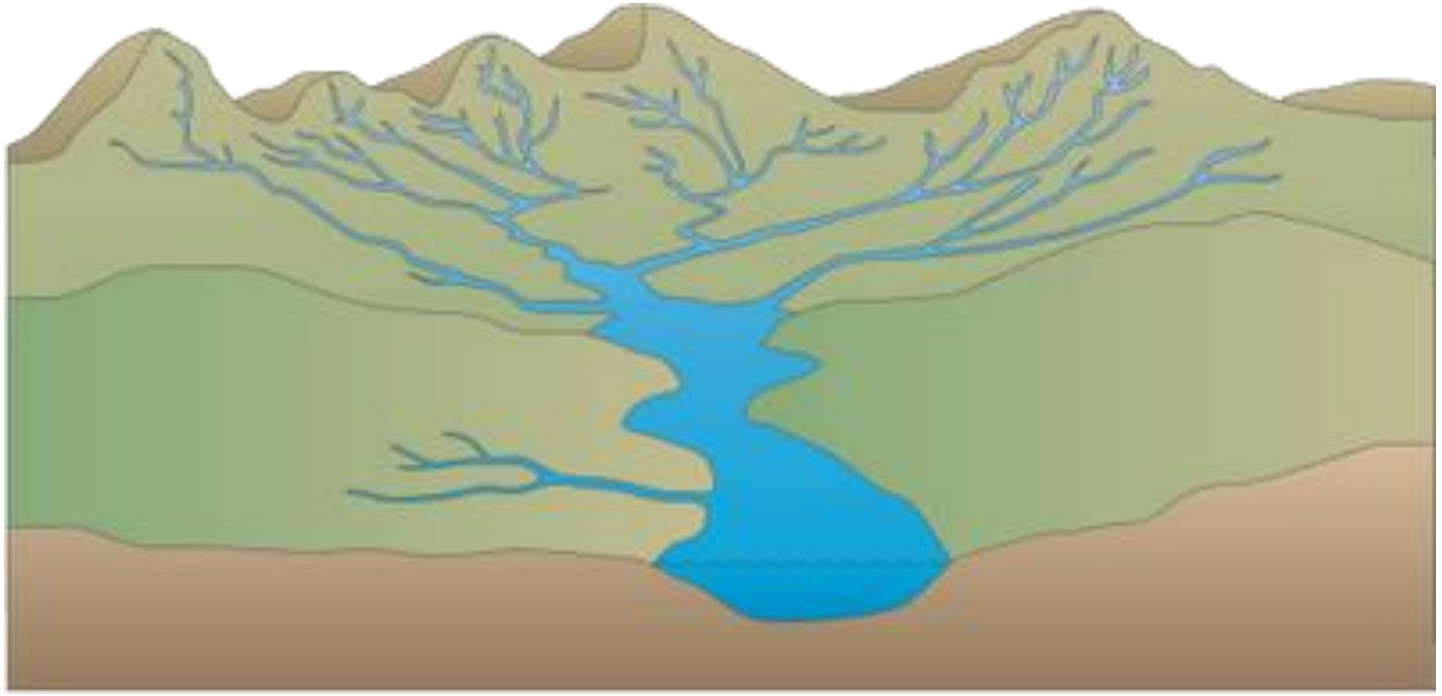
Human activity

- Agriculture, forestry & urbanisation

What is a Catchment?

Catchment (watershed) is the natural area in a landscape that drains surface runoff from precipitation into various inland ecosystems

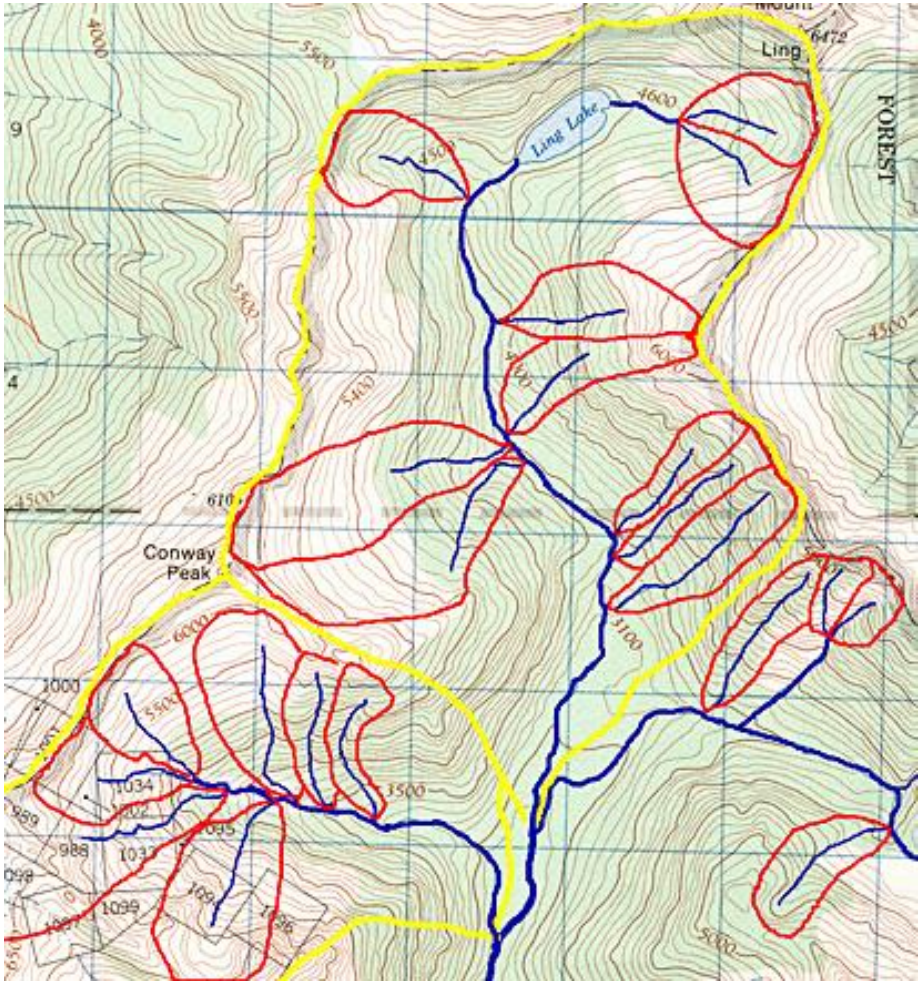
Ridges and hills define water movements within catchments



The geology of the catchment may determine the natural water quality of freshwater wetlands

What Does a Catchment Look Like?

Catchments (watersheds) in yellow with sub-basins in red



What role does catchment geology play?

Importance of Catchment Geology

To understand the chemical composition of the waters within a catchment you must consider the:

- Topography (Practical 1)
- Nature of the vegetation – well vegetated soils are more resistant to erosion (Botany lectures)
- Weathering of the parent rock – freeze-thaw action (Practical 1)
- Climatic factors - strongly influences the rate of weathering and dissolution of minerals

Soil type and **geology** of the catchment have the greatest impacts on water chemistry

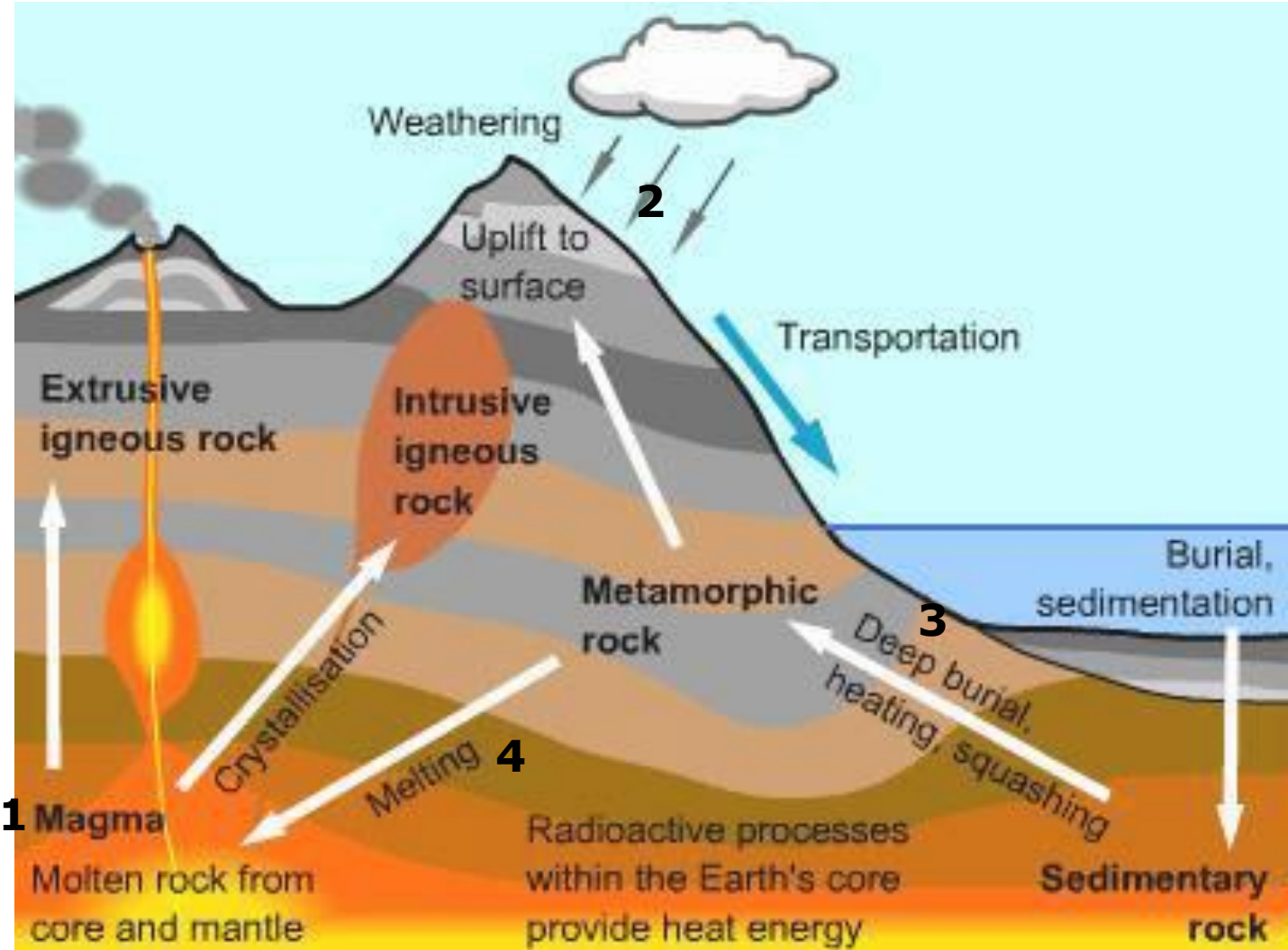
The Rock Cycle

Rocks – all solid materials of the Earth's crust

- Different types are based on characteristic features and origin

4 key processes in rock formations

Three key rock types found worldwide



Characteristics of Rock

Igneous

- 65% of earth's crust
- Develop when liquid molten rock solidifies in/on the earth's surface
- e.g. granite, basalt
- Hard rock
- Acidic

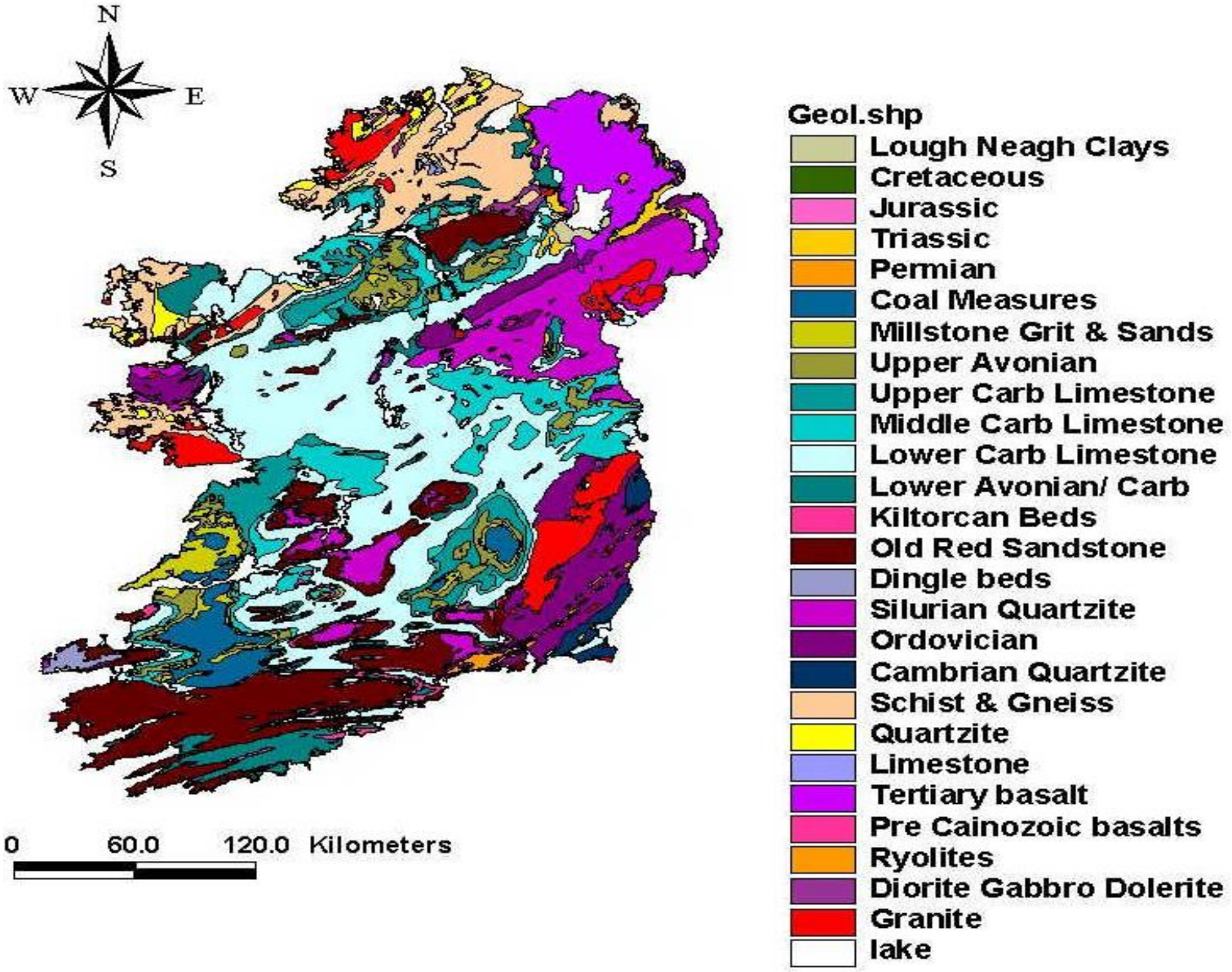
Sedimentary

- 8% of the earth's crust
- Develop on the Earth's surface through accumulating solid matter particles and precipitation of dissolved material at atm. temps. and pressures
- e.g. sandstone, limestone
- Soft rock
- Alkaline

Metamorphic

- 27% of the earth's crust
- Formed when igneous and/or sedimentary rocks are subject to intense heat and/or pressure
- e.g. slate, schists, marble
- Soft rock
- Alkaline

The Geology Map of Ireland

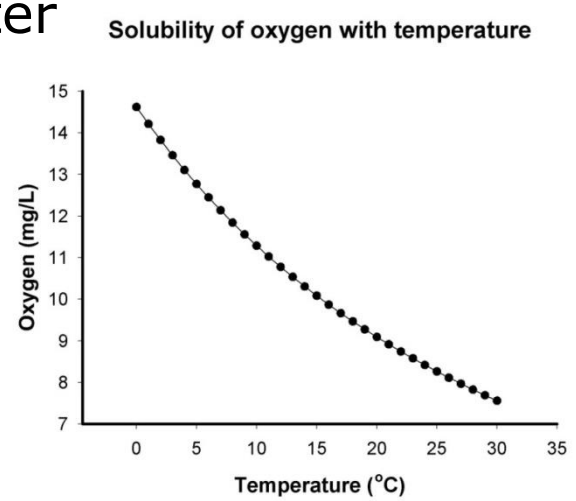


What are the key abiotic factors influenced by catchment characteristics and geology?

1. Dissolved Oxygen (DO)

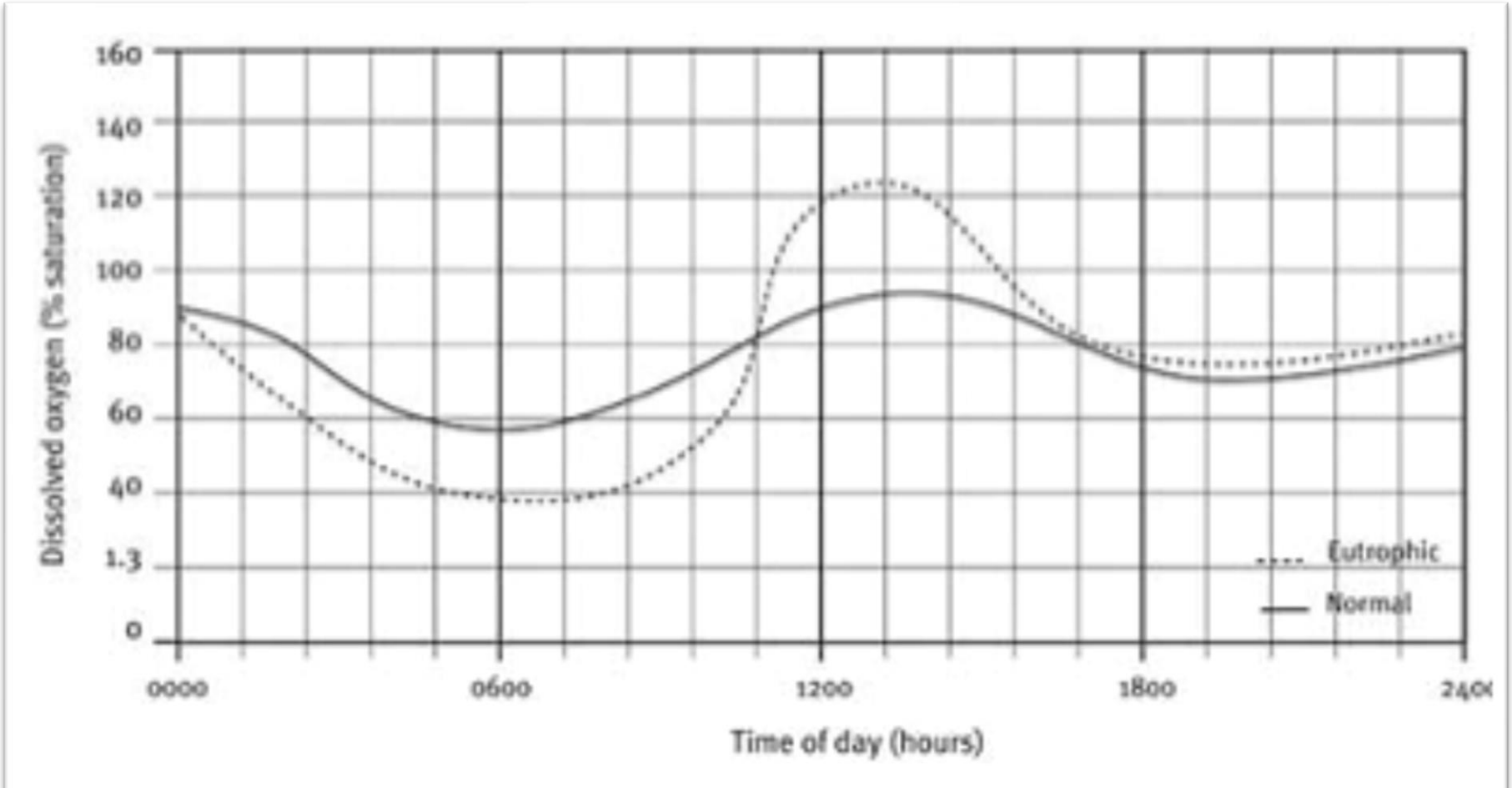
DO - amount of oxygen dissolved in the water column

- Most fundamental parameter of inland waters
- Essential to the metabolism of all aerobic aquatic organisms (aerobic respiration)
- Measured using a DO probe and meter (mg/l and %saturation)
- Should be >8mg/l
- Natural waters are quite low (14mg/l) in oxygen conc.
- High rates of photosynthesis can create conditions of supersaturation (saturation >100%)
- Very little oxygen can actually dissolve in water
  - Dependant on temperature and pressure
  - Turbulence, photosynthesis, respiration, pollution, organic matter, eutrophication
- Oxygen solubility in water is **negatively correlated** with water temperature
- **Oxygen increases in cold waters**



1. Dissolved Oxygen (DO)

Diurnal temperature changes: concs. of oxygen decreases significantly during the night due to respiration



2. pH

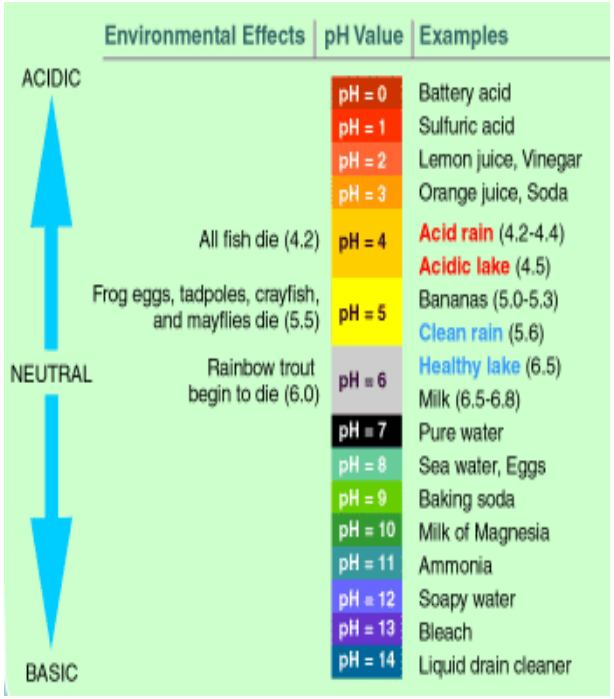
pH = a measure of the concentration of hydrogen ions in solution (H^+)

$$pH = -Log_{10}[H^+]$$

Ranges in scale from 1 - 14

- pH 0 - 7 = Acidic
- pH 7 – 14 = Alkaline
- ~pH 7 = Circum-neutral

$H_2O \rightarrow H^+$ (acidic) + OH^- (basic)



Remember !!

- A change of one pH unit is equivalent to a tenfold change in H^+ **Why ?**
- Increasing H^+ is signified by lower pH values = acidic
- Decreasing H^+ is signified by higher pH values = alkaline

2. pH

In nature, essential minerals and nutrients are always being added or removed from water

- Pure water does not exist in nature
- Rainwater is slightly acid (pH 5.6)
- For freshwater organisms, a pH range from 5.5–8.5 is within which most waterbodies fall
- Living organisms function best between pH 6.5–8.2
- CO_2 from the atmosphere produces carbonic acid which dissolves carbonates acting as a **buffer** neutralising excess acidity
- **Natural buffering capacity** slows the gradual decline in pH to around 6
- However, some freshwaters are naturally acidic e.g. peatland and bog pools
- Hard geology with little weathering of buffering capacity limits the buffering capacity so the excess acidity is not neutralised

3. Carbon Dioxide

CO_2 diffuses into water droplets in the atmosphere and forms weak acid = **carbonic acid**

$$\mathbf{CO_2} + H_2O \Leftrightarrow \mathbf{H_2CO_3}$$

This acid dissociates to form **bicarbonate ions**

$$\mathbf{H_2CO_3} \Leftrightarrow H+ + \mathbf{HCO_3}\text{-}$$

$$\mathbf{CO_2} + H_2O \Leftrightarrow \mathbf{H_2CO_3} \Leftrightarrow H+ + \mathbf{HCO_3}\text{-}$$

Results in natural rain water having a pH of 5.6

Dissolved carbon dioxide and bicarbonate are the primary sources of carbon for photosynthesis and the generation of organic substances

4. Alkalinity

Alkalinity - is a measure of the **buffering capacity** i.e. the capacity of the water to resist changes in pH

- It is also the measure of the concentrations of carbonate and bicarbonate ions in solution (mg/l of equivalent $CaCO_3$ (calcium carbonate))
- Alkalinity **DOES NOT** refer to how alkaline a solution is
- Most buffering systems in natural waters consists of carbonate ions (CO_3^{2-}), bicarbonate ions (HCO_3^-) and hydroxide ions (OH^-)

$$CO_3^{2-} + HCO_3^- + OH^- - H^+$$

- Natural source of alkalinity = catchment geology
  - **Limestone** have good buffering capacity = alkaline
  - **Granites** and **sandstones** have low alkalinity = acidic
- High alkalinity leads to a stable pH regime (up to 400mg$CaCO_3$/l) = Good Buffering Capacity
- Low Alkalinity (<20mg/l $CaCO_3$) = Poor Buffering Capacity
  - Below this level acid shock may occur in some organisms
  - Waters are susceptible to acidification

Carbon Dioxide - pH – Alkalinity

Proportion of free CO_2, CO_3^{2-} and HCO_3^- in water is controlled by pH

When CO_2 is taken up by photosynthesis

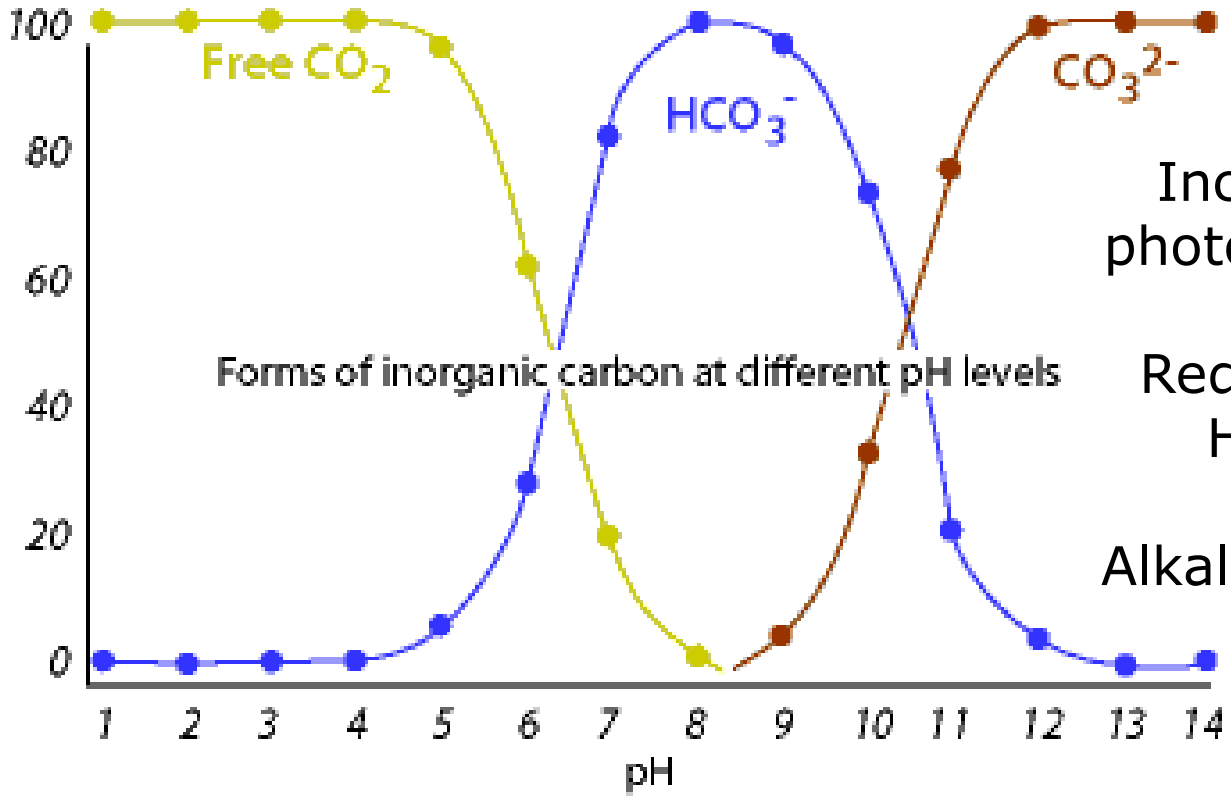
- Free H+ ions are associated with HCO_{3-} and CO_3^{2-}
- Leads to fewer free H^+ = higher pH = alkaline waters
- However, can cause pH fluctuations = stress to aquatic organisms

Respiration adds CO_2 to the system which releases H^+ ions

- Leads to lower pH = acidic waters

Carbon Dioxide - pH – Alkalinity

Increase in respiration = Increase in H^+ ions = Acidic waters



Increase in photosynthesis = Reduction in H^+ ions = Alkaline waters

Respiration

$$\mathbf{CO_2} + H_2O \Leftrightarrow H_2CO_3 \Leftrightarrow H^+ + \mathbf{HCO_3^-} \Leftrightarrow \mathbf{CO_3^{2-}} + 2H^+$$

Photosynthesis

5. Hardness

Hardness - concentration of divalent metal ions expressed as mg $CaCO_3$ /l

- Governed by the amount of **calcium** and **magnesium** combined with bicarbonates and carbonates
- Generally, hardness and alkalinity are similar due to their common sources in limestone areas
- Carbonate hardness can be removed by boiling

Classification of water hardness in Ireland:

0 – 75mg/l	Soft
75 – 150 mg/l	Moderately hard
150 – 300mg/l	Hard
>300mg/l	Very hard

6. Conductivity

Conductivity - a measure of the ability of water to conduct electricity

- Expressed in micro Siemens per centimetre (μS/cm)
- Surrogate measure of salinity
- Reflects ionic content of water

Sources of ions:

- Catchment geology
- Precipitation
- Proximity to the sea
- Activities in catchment

Increasing conductivity signify increasing conc. of dissolved ions = hard water

7. Phosphorus (P)

P in pristine freshwaters is comparatively low = **limits biological productivity in freshwaters**

- P is derived from the weathering of rocks = little bio-available release
- Clay particles in soil bind to P making it resistant to simple leaching via runoff (locks it in)

Two important forms of phosphorous:

1. **Soluble reactive phosphorus** (SRP)/**Phosphate** (PO_4^{3-}) is an approx. measure of available P to living organisms
   - Unpolluted waters ~0.05 mg/l
2. **Total phosphorus** (TP) a measure of the total amount of P potentially available in the water
   - Unpolluted waters ~0.03 mg/l, never >0.05mg/l

8. Nitrogen (N)

Most abundant element in living cells

- 80% air is nitrogen
- Nitrogen gas (N_2) cannot be used directly by most organisms
  - **Nitrogen fixers** e.g. Cyanobacteria, legumes (Fabaceae), alder trees (*Alnus*)

Ammonium and **nitrate** ions are the dominant forms available for uptake by plants

Ammonium (NH_{4+})

- Highly toxic
- Can be retained by soil
- Can be toxic to aquatic plants & animals
- Ranges between 0–2mg/l

Nitrite & Nitrate

- Most abundant forms of combined inorganic carbon in freshwaters
- Range between 0-0.01mg/l and 0–10mg/l respectively

Rule of Thumb

When linking geology with water chemistry within freshwater ecosystems important to remember:

- **Soft waters** = mountain lakes and rivers in resistant, igneous rock (e.g. granite) resemble rainwater in their chemical composition
  - Low levels of dissolved salts
  - Can be acidic

- **Hard waters** = sedimentary rocks (e.g. sandstone and limestone) dissolve more easily
  - Unlike rainwater have high levels of dissolved salts
  - Typically alkaline

Key Points

Water chemistry is affected by catchment characteristics and geology

Oxygen is negatively correlated to temperature

pH measures acidity

Alkalinity measures buffering capacity i.e. carbonate, bicarbonate levels

Hardness measures metal ions (calcium and magnesium ions)

Nitrate, ammonium and phosphate are the dominant nutrient forms available for uptake by freshwater organisms

Reading List

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Freshwater Ecology and Limnology books in the library ;)

Thank you