Phosphorus and Phosphate

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Phosphorus

- Phosphorus is a vital nutrient necessary for plants and animals in the form of $\text{PO}_4^{3-}$ and $\text{HPO}_4^{2-}$.
- Phosphorus is the building block of important parts of the body such as bones and teeth.
- Component in DNA
- About 80% of the world’s phosphorus is used in fertilizers and soft drinks.
Phosphorus

- Unlike other cycles of matter compounds, phosphorus cannot be found in atmosphere as a gas.
- It usually cycles through water, soil, and sediments.
- The phosphorus cycle may also be referred to as the mineral cycle.
Phosphorus Cycle
Phosphorus Cycle

- The phosphorus cycle is the **SLOWEST** cycle.
- Phosphate salts that are released from rocks through weathering usually dissolve in soil water and will be absorbed by plants.
- Animals absorb phosphates by eating plants or plant-eating animals.
- When animals and plants die, phosphates will return to the soils or oceans again during decomposition.
- After that, phosphorus will end up in sediments or rock formations again, remaining there for millions of years. Eventually, phosphorus is released again through weathering and the cycle starts over.
Human Impacts on the Phosphorus Cycle

- Like nitrogen, increased use of fertilizers increases phosphorus runoff into our waterways and contributes to eutrophication.
Step by step eutrophication process
Oligotrophic lake with a low level of nutrients.
Artificial input of nutrients from run-off and discharge of effluent.
Eutrophic lake with a high level of nutrients. Phosphorus is usually the bio-limiting element in freshwater lakes.
Rapid growth of algae and other biomass resulting in a decrease in the concentration of dissolved oxygen.
Turbidity (cloudiness) of water increases as does rate of sedimentation.
Increased growth of rooted plants such as reeds.
Algal blooms during the Summer months. Note that dissolved oxygen levels are at their lowest at night when plants respire rather than photosynthesis.
Development of anoxic conditions and release of noxious gases such as hydrogen sulphide, thioalcohols and ammonia.
The Big Picture

Healthy System
- Balanced Algae Growth
- Adequate Oxygen
- Healthy Bay Grasses

Eutrophic System
- Excessive Nutrient Inputs
- Algal Bloom
- Reduced Bay Grasses
- Algae Die-off
- Algae Decomposition
- No / Low Oxygen

Sunlight

Adapted from a CBP diagram
Effects on water quality

- **Bad taste and odor**: some of the algal species that "bloom" produce toxins (geosmin, MIB), water taste and odor deteriorates.

- **Oxygen depletion**: penetration of light into the water is diminished. This occurs because the algae forms mats as a result of being produced faster than they are consumed. Diminished light penetration decreases the productivity of plants living in the deeper waters and hence their production of oxygen.

- As the water becomes depleted in oxygen, the abundant algae and fish die and decompose, further oxygen is consumed by this process.

- Under anoxic conditions **iron, manganese, ammonia and phosphorous** are released into the water column, anaerobic bacteria flourish, producing **hydrogen sulfide**.
Primary *productivity*

- rate of photosynthesis (carbon-fixing)

Three common productivity levels are indicated in the figure:

- oligotrophic
- mesotrophic
- eutrophic
Ideal Development of Stratification in a Lake

(a) Summer Stratification

- Sunlight
- Wind
- Algal growth
- Epilimnion (20°C)
- Thermocline
- Hypolimnion (10°C)
- Cold, stagnant water
- Low D.O. concentrations
- Best location for water withdrawal

(b) Fall Overturn

- Sunlight
- Wind
- 10°C
- Complete mixing

(c) Winter Stagnation

- Sunlight
- Wind
- Ice cover (0°C)
- No mixing
- 4°C
- Best location for water withdrawal

(d) Spring Overturn

- Sunlight
- Wind
- 4°C
- Complete mixing
- 4°C
Phosphorus in Wastewater

- Orthophosphate
- Condensed phosphates
  - Polyphosphates (linear)
  - Metaphosphates (cyclic)
- Organic phosphates
  - \( R = \text{organic} \)
- Triplyphosphate
- Pyrophosphate
- Trimetaphosphate

E.g., nucleotides, phospholipids, sugar phosphates
Forms of phosphorus found in aqueous solutions

**Orthophosphate**
\[ \text{PO}_4^{3-}, \text{HPO}_4^{2-}, \text{H}_2\text{PO}_4^{-}, \text{H}_3\text{PO}_4 \]

**Polyphosphate**
2 or more P atoms + O₂ atoms + (H) combined in a complex molecule

**Organic Phosphate**
Minor
Phosphorus in wastewater

- Average person releases 1.5 g/day
- Prior to the development of detergents:
  - Inorganic 2-3 mg/L
  - Organic 0.5 – 1 mg/L
- EPA:
  - Sewage effluent should not contain > 1 mg/L
  - Unpolluted waters usually < 0.1 mg/L
Human Impacts

- Heavy-duty synthetic detergents
  - Contain polyphosphates
  - 12-13% phosphorus
- Domestic wastewater
  - 2-3x inorganic P due to detergents
- Municipal wastewater contain 4-16 mg/L phosphorus as P
Polyphosphorus is a builder

- Laundry detergents are formulated from six groups of substances:
  - surfactants
  - builders
  - bleaching-agents
  - enzymes
  - fillers
  - other minor additive

**Builders**

Builders are key detergent components which remove the calcium and magnesium ions present in hard water and in soils, thus lowering the concentration of surfactants necessary to perform the detergents action. Some builders also prevent the deposition of calcium and magnesium salts on fabrics and washing-machines.
* Orthophosphates are available for biological metabolism without further breakdown

Polyphosphate → Orthophosphate
Hydrolysis (slow)

* Organic Phosphate : minor in domestic ww
Methods

Methods:
- Gravimetric ➔ applicable when concentration is high
- Volumetric ➔ when conc. > 50 mg/L
- Colorimetric

- Organic and polyphosphates have to be converted to orthophosphate for measurement
* Orthophosphate determined colorimetrically

* Ammonium molybdate

Colored complex with phosphate at low pH

Polyphosphate analysis ➔ boil the sample (that have been acidified with H₂SO₄) for at least 90 min
Total inorganic phosphate-ortophosphate=poly-P
Phosphorus Determination is important

- Corrosion prevention, control of boiler’s scale
- Assessing the potential biological productivity of surface waters
- Eutrophication control
- WWTP effluents
- Operation of WWTP
- Stream Pollution Control