WATENV – Water and environment

Lecture 9

Please note*: There will be no questions about lecture 8 ("Water engineering – examples: the California Aqueduct construction and the Kissimmee River restoration in Florida") in the test.*

9. Water chemistry

- Due to the differences between physical and chemical properties of water and air,aquatic and terrestrial habitats differ from each other.

Properties of aquatic habitats:

- lower variations of temperature due to the high effective heat capacity of water,
- lower availability of dissolved gases,
- higher density and viscosity,
- primary energy (sunlight) is only available in near-surface water

- Due to their currents, stream systems differ from limnic systems
- **Abiotic locality factors** serve as determining factors for all hydrochemical and photosynthetic processes
- They are prerequisite for the occurences and areal distribution of all macrophytes – and the plant communities consisting of them.
- The combination of factors (interaction of all major factors) defines the habitat.
- Extreme factors have the most selective effects on the habitats
  → only few species are adapted.
- Thus, **extreme locations** are poor in species, but due to the lack of competition rich
- in individuals

9.1. Water as dissolvent and transporting medium

- The quantitative and qualitative availability of essential gases and nutrients in thewater differs from the availability in the terrestrial and atmospheric zone, respectively.
- Solubility behavior, transport and diffusion processes of gases and soluble substances
- are responsible for that.
- Due to its **dipolarity**, water is a good solvant (but: accumulation of difficultly solublecomponents like quartz and heavy metals).
- **Turbulent water movements** (in streams) compensate for slow diffusion rates
- However, through-mixing in water is not as fast as in air due to the higher viscosity of water
- The confluence of two streams with differing amounts of suspended matter shows only a low through-mixing (Good example: Confluence of Amazon River and Rio Negro)

Central factors for water organism's supply with breathing gases and nutrients:

- solubility,
- transport speed,
- turbulent through-mixing.

9.2. Origin and cycles of important elements and compounds

- Essential elements for the metabolism of water plants:
- **macro nutrients**: C, O, H, N, P, S, K, Ca, Mg
- **micro nutrients**: Fe, B, Zn, Cu, Mn, Mo, Cl, Na, Se, Co, Si, J

- **Limiting factors** for the primary production:
- anorganic phosphor molecules,
- anorganic nitrogen molecules,
- anorganic carbon,
- potassium.
- micro nutrients are **no** limiting factors in waters.

- Anthropogenic enrichment of phosphate and nitrate cause a massive increase of
- biomass (**eutrophication**).

9.3. Carbon

- Photoautotrophic organisms need anorganic carbon for primary production
- Phototynthesis equation:
  $6\ CO_2 + 12\ H_2O \xrightarrow{h\nu} C_6H_{12}O_6 + 6\ O_2 + 6\ H_2O$ (hv: sunlight energy)
- Long-term depletion by the formation of **carbon sinks** and CO_2-buildup in deep ocean water
- Currently, **fossile CO** returns into the C-cycle (oil, natural gas, coal)
- In nearly or completely carbonate-free, acid, siliceous or swampy waters, sporadic
- carbonic acid shortages can occur
- **$CaCO_3 + 2H^+ \leftrightarrow CO_2 + Ca^{2+} + H_2O$**
- However, in carbonatic drainage areas, a sufficient concentration is available
- When intensive photosynthesis occurs, the pH value of carbonate-rich waters can reach pH 11 and more than pH 9 in carbonate-poor waters.

9.4. Proton concentration

- **Basic waters** lie in carbonatic drainage areas (high buffering capacity)
- **$CaCO_3 + 2H^+ \leftrightarrow CO_2 + Ca^{2+} + H_2O$**
- Siliceous drainage areas are usually characterized by acid waters (low buffering capacity)
- The **pH value** of waters is subjected to yearly and daily changes.
- The **pH value** indirectly influences form and availability of nutrients.
- Acid waters have only low levels of plant accessible phosphates due to the formation
- of hardly soluble compounds with metal ions at pH values lower than 6

9.5. Humic substances

- Dead organic material is microbially degraded and either completely mineralized or partly dismantled and transformed into **humic substances** by biotic or abiotic processes.
- Humic substances have acid and hydrophilic properties and tend to form chemical complexes.
- Humic substances occur as **fulvic acids** or **humic acids** in waters (Fulvic acids are soluble in water at all pH values, humic acids in water with pH values above 6.5)
- The amount of **dissolved organic carbon (DOC)** in rivers and lakes is 1 to 10 mg/l.
- Humic-rich waters (swamp lakes) can reach up to 30 mg/l DOC.

9.6. Oxygen

- Atmospheric oxygen is mostly a product of photosynthesis.
- Oxygen was released into the atmosphere by **photosynthesis acitivity** over the last ~2.5 billion years
- Oxygen in waters is either dissolved or built into molecules. Its solubility in water is low.
- The oxygen concentration is especially important for the zoogenic elements of the water habitats and determine the species composition as well as the areal distribution of species.
- Oxygen enters the water independently from primary producers by precipitation water and diffusion, depending on the partial pressure difference
- The process is intensified by wind- or stream-induced turbulences at the water surface, and strengthened by the through-mixing of the water body
- Physical input of air into a stream due to turbulent flow
- Depending on the primary production, there can be an oxygen over-saturation in the **trophic** zone of a lake.
- This oxygen is either emitted into the atmosphere or an O_2-over-saturation is established.
- Short- and long-term oxygen concentrations of up to 20 mg/l in the epilimnion arenot unheard of, while the hypolimnion of eutrophic lakes is mostly devoid of oxygen.
- In **oligotrophic** to slightly eutrophic streams, the free-flowing water has an almoststeady oxygen saturation of about 100% at normal illumination conditions.
- Shadowed streams can have a small oxygen undersaturation.
- Non-polluted, shadowed soft water streams are **stenoxic**, meaning only a small variation of the oxygen concentration, less than 10 % a year.
- Complete or near-complete O_2-consumption by biological breathing proceses – measured as „**biological oxygen demand**“ (BOD) in mg/l and abiotic, chemicaloxidation processes, measured as „**chemical oxygen demand**“ (COD) in mg/l – can lead to a devastation of aquatic habtiats.

9.7. Nitrogen

- **Nitrogen** is an essential macro nutrient, existing in almost non-reactive molecular form (N_2) in the atmpsphere with 78,1 volume percent; like carbon mostly originatingfrom **volcanic exhalations**
- Rocks are mostly nitrogen-free. Biogenic fixation and sedimentation of nitrogen containing compounds remove nitrogen from the cycle in the long term.
- Despite the high atmospheric N-concentration, nitrogen is a limiting factor for many plants. Only the anorganic nitrogen compounds nitrate (NO3) and ammoniun (NH4)are plant accessible and therefore potential eutrophication factors.
- Biogenic fixation and transformation into plant accessible forms of nitrogen is accomplished by free-living or symbiotic cyanobacteria, among others the genus *Rhizobium*.
- Permanent mineralization in the aerobic zone and subsequent **denitrification** processes in the anaerobic zone transforms both organic and anorganic N compounds to elementary nitrogen (N_2) that re-enters the atmosphere
- In unpolluted waters, **nitrate** is the major form of nitrogen, and is a growth-limiting factor in oligotrophic sandy areas.
- **Ammonium**, a primary end product of organic N compounds, is – together with nitrate – a major nitrogen source for many hydrophytes.
- Example for nitrogen in the environment: the **Gulf of Mexico Dead Zone**
- Nitrogen fertilizers are massively used by farmers in the watershed of the Mississippi River
- With rainwater, the nutrients are washed into the Mississippi River
- At the river's delta, the nutrients cause excessive algae growth
- The decomposition of dead algae material consumes oxygen, creating a "Dead Zone" in the Gulf of Mexico
- Mississippi River watershed: 2.981.076 km²
- Increase in nutrient-demanding corn cultivation in the USA for biofuel
- Mississippi River flood, May 3, 2011, New Madrid, Missouri
- Flood in spring 2011: the largest Gulf of Mexico Dead Zone on record will result from the flooding
- In May 2011, 164,000 metric tons of nitrogen were transported to the northern Gulf, according to the U.S. Geological Survey – a 35% climb from average May nitrogen estimates in the last 32 years
- The Gulf has seen a 300% increase in nitrogen content since 1960
- Dead zone in 2008, having a size of almost 30,000 km²
- Fish kills close to the Mississippi delta

9.8. Phosphate

- Geogenic: **phosphate**, a macro nutrient, is released by the weathering of the mineral apatite
- Biogenic phosphate returns into the nutrient cycle by mineralization processes.
- Due to the temporary capturing of available phosphates in the biomass, the phosphate concentration in waters shows a typical cycle over a year.

- In unpolluted waters, **phosphate** is the most important production-limiting factor and an important indicator of eutrophication, because even a small increase in concentration can lead to a major increase in phytomass production.
- The very low phosphate concentrations result from anthropogenic inputs (fertilizers) by soil erosion, mineralization processes of dead biomass and release from aquatic
- sediments.
- Like nitrate ions, phosphate ions run through the epilimnic cycle 10 to 40 times during a vegetation period.

9.9. Sulfur

- **Sulfur** is released by exhalation and rock weathering. Its most important oxidation product – **sulfate** – is the second most-abundant anion in waters.
- The natural concentration varies between 5 and 150 mg SO/l in Central European streams.
- Today, sulfate often reaches waters due to anthropogenic activity.
- Especially high concentrations can occur after snow melt due to accumulation.
- In poorly buffered waters this quickly leads to **acidification**, because sulfur dioxide forms sulfuric acids when radicals are present. Their acid rest is sulfate.

9.10. Potassium

- The easiliy soluble **potassium** is released in high amounts by the weathering of layered silicates and feldspars.
- Nevertheless, its availability is limited because the formation of clay minerals consumes high amounts of potassium, thus removing it from the cycle.
- Moreover, its concentration in groundwater and surface water is subjected to strong regional variations.

9.11. Iron

- **Iron** occurs in several compounds in waters and is an essential trace element for plants.
- Naturally increased concentrations occur due to enrichments in the upper layers (hypolimnion) of eutrophic lakes.
- Moreover, increased iron concentrations often occur in mining ponds and the streams originating in them, e.g. in the Lausitz lignite area.
- After groundwater drawdowns in the lowlands of sandy Pleistocene landscapes, high concentrations of Fe^{2+} ions – which are well soluble in oxygen-poor zones – reach the
- surface waters by drainage systems, where they precipitate in the form of red iron hydroxides.
- Small channel in the Hannover Moorgeest, enriched with red iron hydroxides

9.12. Silicon

- **Silicon** is the second most abundant element of the Earth‘s crust, with 27.7 weight percent.

- Thus, silicic acid (H_4SiO_4, $H_3SiO_4^-$) occurs in surface waters with concentrations between 0.15 to 0.65 mmol/l.
- In a certain amount, silicon is deposited in limnic systems as **diatom mud** and thus being removed from the cycle.
- Especially in eutrophic limnic systems in carbonate landscapes, silicon oxides can be
- completely consumed during **diatom blooms** or at least temporarily become a production-limiting factor.

9.13. Chloride

- Easily soluble **chlorides** with small adsorptive bonds reach surface waters by weathering or near coastlines by precipitations and as aerosols, respectively.
- In higher concentrations, chlorides are toxic for most freshwater plants due to their strong osmotic behavior.