Exam Water Quality

Master Civil Engineering and Management

Course code:	201800023
Date:	October 31, 2022
Location:	Therm 2
Time:	13:45-16:45 *(17:30 for students with right of extra time (25%))*
Lecturer:	D.C.M. Augustijn

Type exam: Closed book

Appendix: Information sheet Water Quality

Instructions:

- This exam consists of five (5) questions. The total number of points that can be earned is 50 points. The number of points are indicated per question and sub question. A partly correct answer is awarded part of the allocated points.
- Write the answers on the provided answer sheets. Write your name on each separate sheet. The blank pages in the middle can be used as scrap paper.
- You have 3 hours for the entire exam. Plan your exam well.
- This is a closed book exam, so you are not allowed to use any books or notes, except the information sheet which is handed out at the beginning of the exam.
- You may use dictionaries (no digital versions).
- You may use a (graphical) calculator.
- Answer the questions in English (language errors are not lowering your grade).
- In answering the questions, be concise and clear.
- Hand in the answer sheets, information sheet and these questions, the scrap paper you can take home.

Good Luck!

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1. **EU-Water Framework Directive (5)**
   a. When should the goals of the EU-WFD ultimately be reached? (1) [22%]
   2027
   b. Is groundwater part of the EU-WFD? (1) [87%]
   Yes
   c. What is meant by the stand still principle? (1) [35%]
   The water quality is not allowed the get worse, it should at least remain the same.
   d. Why are nutrients not priority pollutants? (2) [4%]
   It is difficult to define general rules for nutrients. Each ecosystem/water body has its own (natural) requirements regarding nutrients. Therefore, member states can define their own targets for certain water bodies.

2. **Waste water treatment (13)**
   a. Who is responsible for the waste water treatment in the Netherlands? (1) [63%]
   Waterboards
   b. Why does a separated sewer system (rainwater separated from waste water) make a waste water treatment plant more efficient? (2) [89%]
   The flow of waste water from households and industry is more steady and concentrated making the treatment more efficient.
   c. What are the two main steps in waste water treatment? (2) [59%]
      1. Mechanical treatment (sieving, settling, removal of undissolved substances),
      2. Biological treatment (active sludge, biological degradation of organic matter (BOD) and uptake of dissolved substances)
   d. How is phosphate removed during the traditional treatment process? (2) [21%]
   Phosphate is taken up by activated sludge as part of the assimilation process and incorporated in the biomass of the activated sludge.

   When the phosphate concentration at the end of the treatment process is still too high, iron(III)chloride ($FeCl_3$) could be added to precipitate the access phosphate as iron(III)phosphate ($FePO_4$) according to the following reaction:

   $$FeCl_3 + PO_4^{3-} \rightleftarrows FePO_4 + 3Cl^-$$

   e. Assume a concentration of 0.5 mg/l of PO_4^{3-} in the water at the end of the treatment process. How many grams of $FeCl_3$ need to be added to 1 liter water to precipitate all phosphate? Assume $FePO_4$ is insoluble and $FeCl_3$ is completely soluble. (3) [86%]

Molar mass if PO_4^{3-} is: 95 g/mol
Molar mass if $FeCl_3$ is: 162.2 g/mol
0.5 mg/l = $5 \cdot 10^{-4}$ g/l = $5 \cdot 10^{-4}$ g/l/ 95 g/mol = $5.2 \cdot 10^{-6}$ mol/l
For the precipitation of 1 mole PO_4^{3-} is 1 mole $FeCl_3$ required,
Hence for the precipitation of 1 mole PO_4^{3-} is 1 mole $FeCl_3$ required
$5.2 \cdot 10^{-6}$ $FeCl_3$ is $5.2 \cdot 10^{-6} \cdot 162.2 = 8.5 \cdot 10^{-4}$ g/l = 0.85 mg/l.
Simply: 0.5*162.2/95 = 0.85 mg/l

f. Show that $FePO_4$ indeed has a low solubility by calculating how much $FePO_4$ can dissolve in 1 liter water under standard conditions. Use the following values for the Gibbs free energy: $\Delta G_f^0(FePO_4)$ = -1146.6 kJ/mol, $\Delta G_f^0(Fe^{3+})$ = -4.6 kJ/mol, $\Delta G_f^0(PO_4^{3-})$ = -1018.8 kJ/mol. (3) [60%]
$FePO_4 \rightleftarrows Fe^{3+} + PO_4^{3-}$
$\Delta G_r^0 = \Delta G_f^0(Fe^{3+}) + \Delta G_f^0(PO_4^{3-}) - \Delta G_f^0(FePO_4)$
ΔG_r^0 = -4.6 + -1018.8 - -1146.6 = 123.2 kJ/mol
$K = \exp\left(-\frac{\Delta G_r^0}{RT}\right) = \exp\left(-\frac{123.200}{8.314 \cdot 298}\right) = 2.5 \cdot 10^{-22}$
$K = [Fe^{3+}][PO_4^{3-}] = x \cdot x = x^2 = 2.5 \cdot 10^{-22}$
$x = 1.6 \cdot 10^{-11}$ mol/l
Molar mass $FePO_4$ is 150.8 g/mol, so $1.6 \cdot 10^{-11}$ mol/l is $1.6 \cdot 10^{-11} \cdot 150.8 = 2.4 \cdot 10^{-9}$ g/l = $2.4 \cdot 10^{-6}$ mg/l, this is very small. So $FePO_4$ is nearly insoluble.

3. Water quality data in a river (8)
The figures below show the annual variations averaged over three decades [1990-1999 (blue lines), 2000-2009 (red lines) and 2010-2019 (green lines)] of four water quality parameters [pH, electrical conductivity (EC), oxygen and chloropyll-a] measured in the river Moselle at Palzem in Germany on the border with Luxemburg. The Moselle is a tributary of the Rhine originating in the Vosges, France. The discharge is measured just upstream of Palzem in Perl and shows data for one extra decade. (source: Franzaring, 2022)

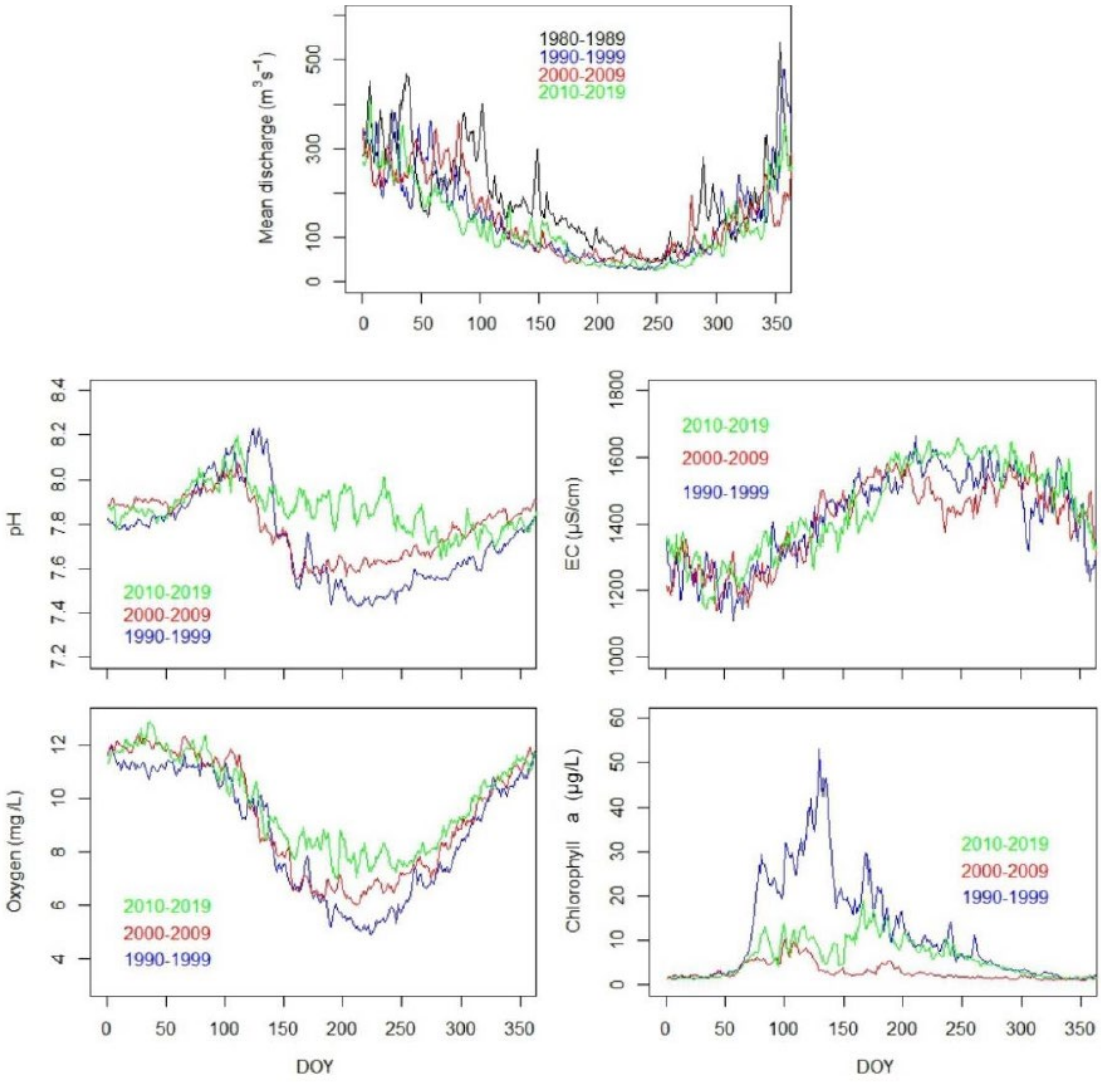
a. Explain the lower concentrations of oxygen in summer. (2) [33%]
The solubility of oxygen is lower at higher temperatures (in summer). [partial points if said more biological activity (decay/respiration) in summer due to higher temperatures]

b. What does the electrical conductivity (EC) represent? (2) [41%]
This represents the concentration of ions (salt) (p. 52 reader)

c. Explain the changes of EC over a year. (2) [23%]
Salts come mainly from (industrial) discharges (point source) which are more or less constant. When the discharge increases due to rainfall (which is relatively clean) the concentration drops. At low discharges, point sources contribute more and EC is higher.

d. Explain the changes in pH related to the chlorophyll-a concentration. (2) [33%]
When the chlorophyll-a concentration increases, more photosynthesis takes place, i.e. CO_2 is consumed and O_2 is produced [this does not explain changes in oxygen concentration in question 3a]. During photosynthesis CO_2 is removed which decreases the concentration of the

weak acid H_2CO_3, increasing the pH (reader p. 51/52+57). [During photosynthesis also H^+ is used, increasing the pH (reaction 3.7, p. 57).]



4. Denitrification in a pond (15)

Assume an urban pond with no in- and outflow. The pond contains a certain amount of nitrate (NO_3^-).

a. What could be the sources of nitrate in such a pond? (2) [93%]

Atmospheric deposition, litter (e.g. leaves) falling into the pond, local runoff or groundwater seepage.

The water in the sediment is anaerobe and there the nitrate is denitrified.

b. To what form of nitrogen is nitrate converted during the denitrification process? (1) [43%]

N_2 [denitrification reaction: $2NO_3^- + 10e^- + 12H^+ \rightleftarrows N_2 + 6H_2O$]

The exchange of nitrate between the water in the pond (C_P) and the water in the sediment (C_S) can be described by a nonequilibrium process (with k_1). The loss of nitrogen by the denitrification process can be described by a first-order decay rate (with k_2). Assume no input of nitrate into the pond for this problem. The volume of the pond is V_P and the volume of water in the sediment in which the denitrification takes place is V_S.

c. Describe the change in C_P as a function of time in a differential equation. (2) [51%]

Denitrification takes place in the anaerobic water in sediment. The total mass balance reads:

$$\frac{\partial M}{\partial t} = V_p \frac{\partial C_p}{\partial t} + V_s \frac{\partial C_s}{\partial t} = -k_2 V_s C_s$$

The exchange of mass between the pond and the water in the sediment is described by a nonequilibrium process:

$$\frac{\partial C_p}{\partial t} = -k_1 (C_p - C_s)$$

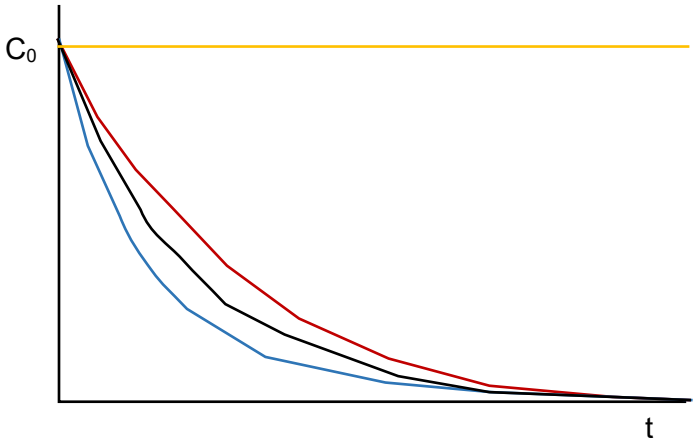
The concentration in the pond decreases when $C_p > C_s$ or increases when $C_p < C_s$. There is no exchange (equilibrium) when $C_p = C_s$. Substitution of the second equation in the first yields:

$$V_s \frac{\partial C_s}{\partial t} = k_1 V_p (C_p - C_s) - k_2 V_s C_s$$

d. Describe the change in C_S as a function of time in a differential equation. (2) See above. [38%]

Assume that the initial concentration of nitrate in the pond and sediment are in equilibrium and equal to C_0. Draw the following answers in the same figure. Make sure the differences are clearly visible.

e. Draw in a figure C_P as a function of time. (2) red [62%]
f. Draw in the same figure C_S as a function of time. (2) blue (C_s is lower because decay takes place in sediment, mass is transferred from pond to sediment because of concentration difference) [26%]
g. Draw in the same figure C_P and C_S when $k_1 \rightarrow \infty$. (2) black (exchange between pond and sediment is very fast (instantaneous) $\rightarrow C_s = C_p$) [27%]
h. Draw in the same figure C_P and C_S when $k_2 \rightarrow 0$. (2) orange (there is no decay, concentrations do not change compared to initial condition: $C_s = C_p = C_0$) [54%]



5. Water quality standards (9)

Arsenic (As) is a heavy metal that is used to treat wood to prevent it from rotting. The maximum permissible concentration (MPC) for arsenic in water is 25 μg/L, the background concentration in water is 0.77 μg/L. The log K value for the adsorption coefficient to sediment is 3.82, with K in L/kg. The background concentration of arsenic in sediment is 29 mg/kg.

a. Calculate the standards (MPC and NC) for Arsenic in sediment in mg/kg. (3) [67%]

$MPC = MPA + C_b \rightarrow MPA = MPC - C_b = 25 - 0.77 = 24.23$ μg/L

$Log\ K = 3.82 \rightarrow K = 10^{3.82} = 6607$ L/kg

$MPA*K = 24.23$ μg/L*6607 L/kg = 160087 μg/kg = 160 mg/kg

$MPC_{sed} = MPA_{sed} + C_{b,sed} = 160 + 29 = 189$ mg/kg

$NC_{sed} = MPA_{sed}/100 + C_{b,sed} = 1.6 + 29 = 30.6$ mg/kg

b. The log K value is based on standard sediment of 10% organic matter and 25% clay. What if the sediment in a particular system contains less organic matter or clay, would the acceptable concentration in sediment be lower, the same or higher than calculated in a? Explain briefly why. (2) [48%]

Lower, because the equilibrium concentration in sediment with the water quality standard concentration in water (MPA) will be lower (K would be lower).

c. What is the difference in meaning of MPC and NC? (2) [80%]

MPC is based on NOEC values (data) and a protection of 95% of the species, NC takes into account all the uncertainties related to this. MPC is for short to intermediate term, the negligible or target concentration is the long-term water quality standard or target concentration.

d. Give two reasons why species might be more sensitive to a certain contaminant in the field than in the lab? (2) [82%]

When the conditions are not optimal for the organism they are more susceptible to negative effects of contaminants. Hence, other stress factors such as the presence of other contaminants (combination toxicity), limited food availability, limited light availability (e.g. for plants/algae), suboptimal

temperatures (too cold/too warm, (strong) variations), salinity, etc. increases the sensitivity to a certain contaminant.