Exam Water Quality

Master Civil Engineering and Management

Course code:	201800023
Date:	November 1, 2021
Location:	SC1
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 six (6) questions. The total number of points that can be earned is 60 points. The number of points are indicated per question and subquestion. 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!

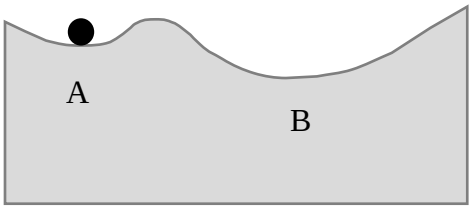
1. **Water quality policy (6)**
   a. Give two aims of the EU Water Framework Directive (WFD)? (2) [82%]
      - Expanding the scope of water protection to all waters, surface waters and groundwater
      - Achieving 'good status' for all waters by set deadline
      - Water management based on river basins
      - Combined approach of emmission limits and quality standards
      - Getting the prices right
      - Getting the citizens more involved
      - Streamlining European legislation

   b. True or false? (2) [88%]
      - A good chemical status by meeting the standards for priority pollutants does only apply to surface waters, not to groundwater. False
      - There are no legally binding standards for pharmaceuticals. True

   c. Give two examples of how an industry can be persuaded to reduce its emissions to the environment? (2) [95%]
      Economic, communication, legal means (legislation)
      - Tax benefits, subsidies
      - Awareness, attitude change, corporate vision, agreements
      - Permits
      - Fines

2. **Eutrophication (13)**
   a. What is meant by an oligotrophic water system? (1) [84%]
      Nutrient poor system
   b. The mole ratio of N:P in biomass is approximately 16:1. If the mole ratio of N:P in water is 25:2, which element is limiting? (2) [85%]
      N
   c. Give three sources of nitrogen and indicate the main source for the Netherlands? (3) [78%]
      Agriculture (manure/fertilizers) 55%, WWTP 14%, atmosphere 24%. Percentages are for the Netherlands (Summary River basin management plans 2016-2021).
   d. What are the two most common forms of dissolved nitrogen in aqueous systems that can be taken up as nutrients by plants and algae? (1) [84%]
      NH_4^+(ammonium) and NO_3^- (nitrate)

Scheffer et al. (2001) depict multiple stable states by marbles in a stability landscape (see below).



e. What do the two valleys represent in relation to eutrophication? (2) [28%]
Two stable states at the same (relatively high) nutrient level: less turbid system with plants and turbid system without plants

f. Which state (A or B) in this figure is most resilient? Explain briefly why. (2) [66%]
State B is most resilient. It takes more effort to push the ball over the top (deeper).

3. pH-Eh diagram Sulfur (9)

The oxidation of organic matter (CH_2O) is a redox reaction. Oxygen is the primary electron acceptor (oxidant). However, under anaerobic conditions bacteria can use other elements as electron acceptors such as sulfate. Sulfate (SO_4^{2-}) in water will be reduced under anaerobic conditions according to the following reaction:

$SO_4^{2-} + 8e^- + 10H^+ \rightleftarrows H_2S_{(aq)} + 4H_2O \qquad Eh^0 = 0.3\ V$

$\Delta G_r^0 = \Delta G_f^0(H_2S) + 4\Delta G_f^0(H_2O) - \Delta G_f^0(SO_4^{2-}) - 10\Delta G_f^0(H^+)$ = -27.87 – 4*237.18 +741.99 - 10*0 = -234.6 kJ/mole

$Eh^0 = -\frac{\Delta G_r^0}{nF} = +234.6 \cdot 10^3/(8*9.6 \cdot 10^4) = 0.3\ V$

a. What is the oxidation half reaction that provides the electrons for this reaction? (2) [14%]

$CH_2O + H_2O \rightleftarrows CO_2 + 4H^+ + 4e$

b. Give two other elements (molecules) that can be used as electron acceptors by bacteria to obtain energy from organic matter decomposition under anaerobic conditions. (2) [75%]
NO_3^- (nitrate), Mn (manganese), Fe (iron), fermentation.

Copy the figure below on your answer sheet

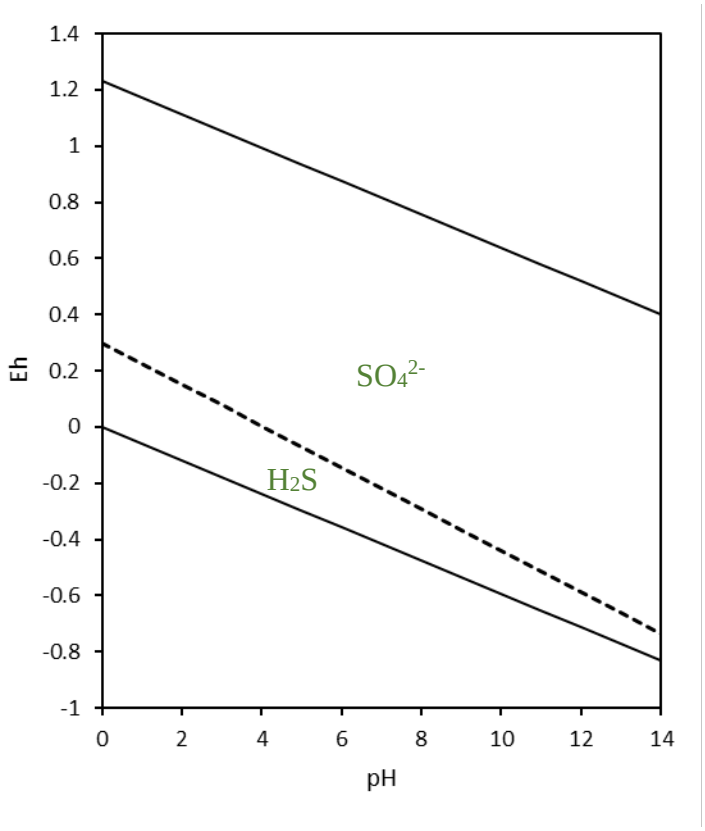
c. Draw in the figure, the line at which the sulfate concentration is equal to the concentration of hydrogen sulfide ($H_2S_{(aq)}$). Indicate in the figure on what side of the line sulfate is the dominant species and on what side hydrogen sulfide is the dominant. Use the Nernst equation for this. (4) [84%]

$$Eh = Eh^0 - \frac{RT}{nF}\, ln \frac{[\text{Red}]}{[\text{Ox}]} \qquad (2.20)$$

$$Eh = Eh^0 - \frac{RT}{nF}\, ln \frac{[H_2S]}{[SO_4^{2-}][H^+]^{10}} = 0.3 - \frac{8.3 \cdot 298}{8 \cdot 9.6 \cdot 10^4} \cdot 2.3 \left(\log \frac{[H_2S]}{[SO_4^{2-}]} - 10 \log [H^+] \right)$$

$[SO_4^{2-}] = [H_2S]$

$Eh = 0.3 - 0.0074(0 + 10\text{pH}) = = 0.3 - 0.074$ pH (dashed line)



d. What is characteristic for this process, in other words, how can you tell sulfate is being reduced? (1) [63%]
Smell like rotten eggs.

4. Polluted lake (14)

A lake is polluted. The contaminant is adsorbed onto the sediment and is not degraded. Initially the concentration of the contaminant in the water column and the sediment are at equilibrium. The volume of the lake V is 10^6 m^3, the

adsorption coefficient K is 0.1 l/g and the mass of the sediment contaminated m is $5 \cdot 10^6$ kg.

Assume average depth is 5 m. Surface area lake is $10^6/5 = 200{,}000$ m^2 (20 ha). 2 cm of the sediment is contaminated = 4000 m^3 sediment. Assume density sediment of 1200 kg/m^3. This is $4.8 \cdot 10^6$ kg sediment.

a. What fraction of the total mass in the lake is adsorbed to the sediment? (3) [74%]
   M = VC +mS = VC + mKC = (V + mk)C
   Fraction adsorbed: mKC/(V+mK)C = mK/(V+mK) = $5 \cdot 10^6 \cdot 0.1/(10^6 + 5 \cdot 10^6 \cdot 0.1)$ =0.33 (1/3)

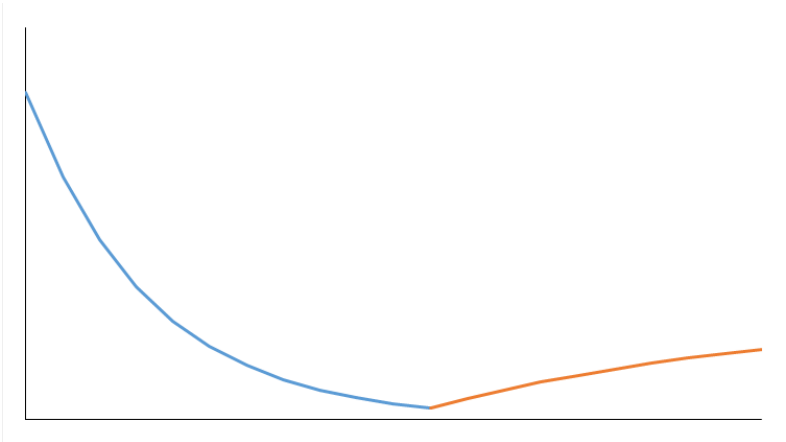
To clean up the lake, the lake is flushed with water that is free of the contaminant. The desorption of the contaminant from the sediment to the water phase is a non-equilibrium process. Assume the lake can be considered a continuously stirred tank reactor.

b. Write the mass balance for the mass of the contaminant in the water phase and the mass balance for the contaminant in the sediment phase (4) [52%]
   $\frac{\partial M}{\partial t} = V\frac{\partial C}{\partial t} + m\frac{\partial S}{\partial t} = -QC$

For the sediment phase: $\frac{\partial S}{\partial t} = k\left(S_{eq} - S\right) = k(KC - S)$

For the water phase: $V\frac{\partial C}{\partial t} = -QC - m\frac{\partial S}{\partial t} = -QC - mk(KC - S)$

c. Draw in a graph the change in concentration as a function if time. (2) (blue line) [78%]



When the concentration in the water column has reached an acceptable level, the flushing of the lake is stopped.

d. Give two parameters that determine the time it takes to reach this acceptable concentration in the water of the lake, and indicate how the parameter affects the time. (Does the time increase or decrease when the value of the parameter increases or decreases?) (2) [90%]

Q and k are the most obvious ones
If Q increases it will reach acceptable concentrations faster.
If k increases it will take longer to reach acceptable concentrations.
(m, K, and V also have an effect on time to reach acceptable concentrations: m and K larger, more mass on adsorbed phase, it will take longer to reach acceptable levels, V larger means more mass in water phase so flushing is more effective, acceptable levels are reached faster).

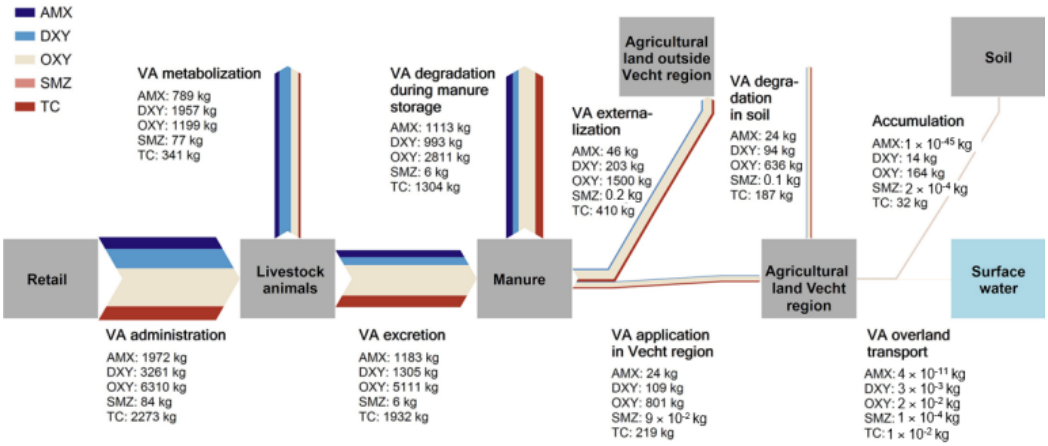
At the time the flushing is stopped there is no flow in or out of the lake any more. There is, however, still a considerable amount of contaminant adsorbed to the sediment.

e. How does the concentration in the water column change as a function of time after the flushing has stopped? Draw this in the same graph as for answer c. Clearly indicate where the answer to this question starts. (2) (see orange line in figure) [81%]

f. Give an example of a measure that could be taken to speed up the remediation of the lake. Does this measure also have disadvantages and can you name them? (3) [81%]
Dredging the lake. This is very disruptive for aquatic live, very costly and contaminated sediment can be hazardous waste.

5. Pharmaceuticals (7)

a. Draw a flow diagram of the pathways of veterinary pharmaceuticals from the supply to animals to surface water. Indicate per step the possible losses. (5) [73%]



b. What measure, given the current use of veterinary pharmaceuticals, is most effective in reducing the emissions to the environment? (2) [55%]
Storage and treatment of manure (e.g. composting) is very effective.

6. Water quality standards (4)

For Chromium(III) the average value of the log(NOEC) is 2.35 with a standard deviation of 0.46. The background concentration of Cr(III) is 0.17 μg/L.

Calculate the maximum permissible concentration (MPC) and negligible concentration (NC) for Chromium(III). (4) [64%]

$F(x) = \frac{1}{1+\exp((\alpha-x)/\beta)}$ and $\beta = \frac{\sigma\sqrt{3}}{\pi}$

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α = 2.35, $\beta = \frac{\sigma\sqrt{3}}{\pi} = \frac{0.46\sqrt{3}}{\pi}$= 0.25

$x = \alpha - \beta\ ln\left(\frac{1}{F(x)} - 1\right)$

F(x) = 0.05 → x = log(NOEC) = 1.61
MPA = $10^{1.61}$ = 40.7 μg/l
MPC = MPA + C_b = 40.7 + 0.17 = 40.9 μg/l

NC = MPA/100 + C_b = 0.41 + 0.17 = 0.58 μg/l