Water and wastewater treatment – Homework 6 - Solutions

1. Water resources quality

The Tables below show the water composition of two raw waters used for drinking water production. Assess the water quality in terms of the Swiss drinking water regulations. Also try to identify the possible water resource of these waters.

Water type 1

Parameter	Measured value
Temperature	7-12°C
pH	6.4-7.1
DOC	1-5 mg/L
UV (254 nm)	1.3-19.5 m^{-1}
Calcium	122 mg/L
Magnesium	3.5 mg/L
Nitrate as NO_3^-	25 mg/L
Atrazine	150 ng/L
Tetrachlorethylene	20 µg/L
Trichlorethylene	15 µg/L
Bromide	20 µg/L
Turbidity FTU	0.2 - 150

Discussion of water quality for water type 1:

T: varies, however, not dramatically. A temperature of around 10°C is well suited for drinking water purposes. The water has to be from a groundwater or a lake water source (lower levels) and excludes a river water.

pH: It can be low at times. It seems not so well buffered.

DOC: highly variable and very high. DOC concentration should be below 2 mg/L for a good drinking water. This points towards seasonal variations or changes due to extreme events (e.g. heavy rainfalls). This points towards either eutrophic lake water or a karstic water.

UV: Follows same trend as DOC. UV is often used as a proxy for the DOC concentration.

Calcium and Magnesium: The water is quite hard, with a Calcium hardness of about 30 °F : 122 mg/L Ca ≈ 3 mM. 1°F = 0.1mM $CaCO_3$ => 3mM Ca = 30 °F

Nitrate: At the quality goal of drinking water.

Atrazine: Atrazine is above the drinking water standard of 100 ng/L. This is an indicator for agricultural activity. Typically atrazine is much higher in groundwaters than in lake waters.

Tetrachloroethylene, trichloroethylene: They are above the drinking water guidelines. They are typical groundwater contaminants.
Bromide: Bromide concentration is low and not regulated.
Turbidity: Turbidity is highly variable and sometimes significantly above the drinking water standard of 1. This points to a source that is closely connected to a surface water.
Overall, the water resource has a character of a groundwater with high hardness but also high variability of DOC and turbidity. This connection points towards a carstic water in a limestone environment. The source water is from the Jura.

Water type 2

Parameter	Measured value
Temperature	11.4^{o}C
pH	7.1
DOC	4 mg/L
Total Hardness ^{o}F	39
Calcium Hardness ^{o}F	35
Magnesium Hardness ^{o}F	3.9
Oxygen	0 mg/L
Nitrate as N	< 0.01 mg/L
Nitrite as N	0.02 mg/L
Ammonium as N	1.2 mg/L
Iron	6.6 mg/L
Manganese	0.22 mg/L

Discussion of water quality for water type 2:
T: Temperature is constant and suitable for drinking water purposes. The water has to be from a groundwater or a lake water source (lower levels) and excludes a river water.
pH: Stable and okay for drinking water purposes.
DOC: Very high. DOC concentration should be below 2 mg/L for a good drinking water. This points towards a eutrophic lake or a groundwater influenced by organic rich soil.
Hardness: The water is hard. This points towards a groundwater.
Oxygen: The oxygen concentration is 0. This points towards a reduced groundwater. This is in agreement with the high DOC concentration.
Nitrogen species: Nitrate concentration is below the detection limit, some nitrite can be found => reduced water resource. Ammonia confirms this finding. It is a result of nitrate reduction.

Iron, manganese: Both metal ions are significantly above the drinking water standard. This confirms that it must be a reduced water resource.
Overall, the water resource has a character of a reduced groundwater with high hardness.

2. Riverbank filtration

Mixing and Transformation processes

A river water (20°C) infiltrates according to the scheme below. Thereby, as a function of the infiltration distance, the mixing ratio with groundwater increases. The two waters differ in their chloride concentration: river water 0.1 mM, groundwater 0.3 mM.

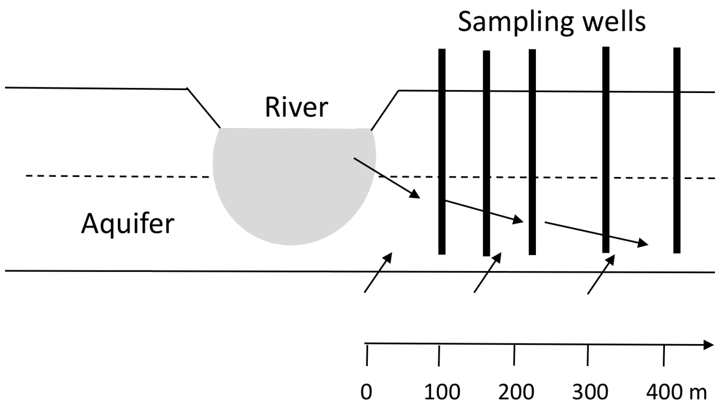


Table 1 shows the measured chloride concentrations in sampling wells as a function of the infiltration distance.

Table 1. Water quality parameters as a function of the infiltration distance

Infiltration distance m	Chloride concentration mM	O_2 mM	NO_3^- mM	SO_4^{2-} mM	HCO_3^- mM	Ca^{2+} mM	pH
0	0.1	0.25	0.4	0.5	2	0.9	7.7
20	0.104	0.05	0.25	0.49	2.4	1.15	7.4
80	0.11	0.02	0.054	0.485	2.6	1.3	7.5
90	0.12		0.04	0.46			
140	0.14			0.44			
250	0.3	0.15	0.2	0.2	2.6	1.3	7.5

a) Based on the chloride concentrations, sketch the relative contribution of river water in the groundwater.
Mixing of water:
The groundwater has two end members, river water and groundwater which have distinctly different chloride concentrations (river water 0.1 mM, groundwater 0.3 mM).

The chloride composition at any point can be approximated by the relative contribution of each end member:

$[Cl]_{tot} = x\,[Cl]_1 + (1-x)\,[Cl]_2$

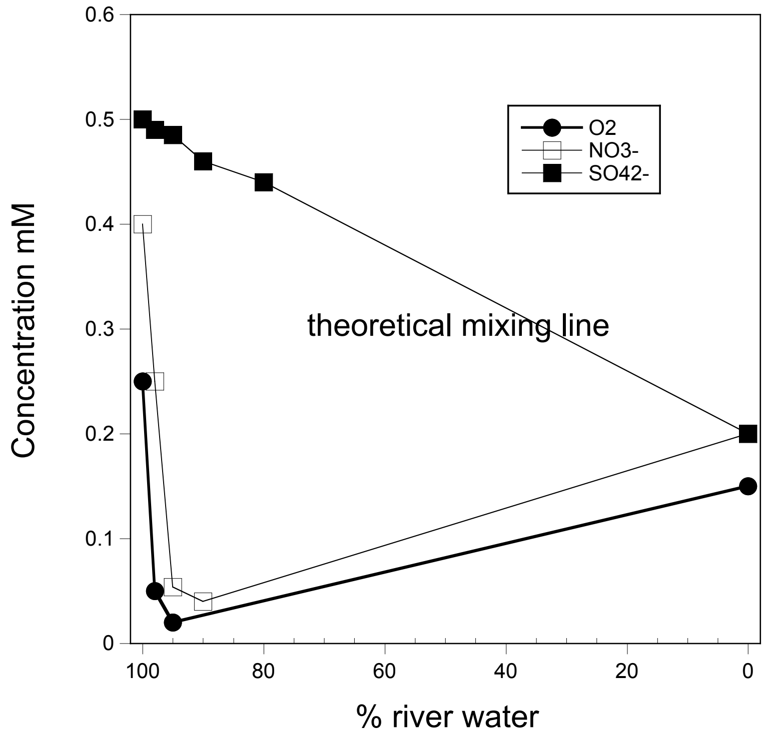
where x is the contribution of river water and 1-x is the contribution of groundwater.

$$x = \frac{[Cl]_{tot} - [Cl]_2}{[Cl]_1 - [Cl]_2}$$

The contribution of river water is shown in the table below

Infiltration distance m	Contribution of river water %
0	100
20	98
80	95
90	90
140	80
250	0

b) The information from the chloride profile can now be used to estimate whether a concentration-distance profile for a given redox-sensitive species (O_2, NO_3^-, SO_4^{2-}) is caused by chemical/microbiological processes or by dilution. Sketch the concentrations of the redox-sensitive parameters as a function of the river water content. What can be deduced from such graphs?



Oxygen and nitrate behave differently than what would be expected from a mixing of the two end members. In this case microbial consumption leads to the fast decrease. The sulfate concentration lies on the theoretical mixing curve. In this case the decrease in the concentration is just dilution and not microbial transformation.

c) Is the $CaCO_3$ equilibrium fulfilled at each sampling well or do we expect a precipitation of $CaCO_3$ upon contact with the atmosphere (what is pCO_2 compared to the atmosphere)? $pK_{so} = 8.39$, pK_1 (H_2CO_3*) = 6.4, pK_2 (HCO_3^-) = 10.2, $K_H = 3.39 \times 10^{-2}$ M atm^{-1}.

The ion activity product (IAP) $[Ca^{2+}][CO_3^{2-}]$ has to be calculated and compared to the solubility product K_{so}. The following conclusions can be drawn:

IAP > K_{so} : oversaturation

IAP = K_{so}: equilibrium

IAP < K_{so}: undersaturation (corrosive water)

In Table 1, $[Ca^{2+}]$, $[HCO_3^-]$ and pH are given. Therefore the IAP can be calculated as follows:

$$\left[Ca^{2+}\right]\left[CO_3^{2-}\right] = \frac{K_2\left[Ca^{2+}\right]\left[HCO_3^-\right]}{\left[H^+\right]}$$

Infiltration distance m	$[Ca^{2+}][CO_3^{2-}]$ -log IAP
0	8.24
20	8.36
80	8.17
90	
140	
250	8.17

The water is oversaturated with regard to $CaCO_3$ at all sampling points. Such deviations from the equilibrium are not uncommon. The water has a slight tendency to precipitate $CaCO_3$. This is actually desired from a point of view of corrosion control in the distribution system.
To assess the potential for precipitation, the CO_2 partial pressure has to be calculated.
The carbonic acid concentration $[H_2CO_3^*]$ is related to pCO_2 by the Henry constant:

$[H_2CO_3^*] = k_H pCO_2$

$[H_2CO_3^*]$ can be calculated from $[HCO_3^-]$ and pH:

$$[H_2CO_3 *] = \frac{[HCO_3^-][H^+]}{K_1}$$

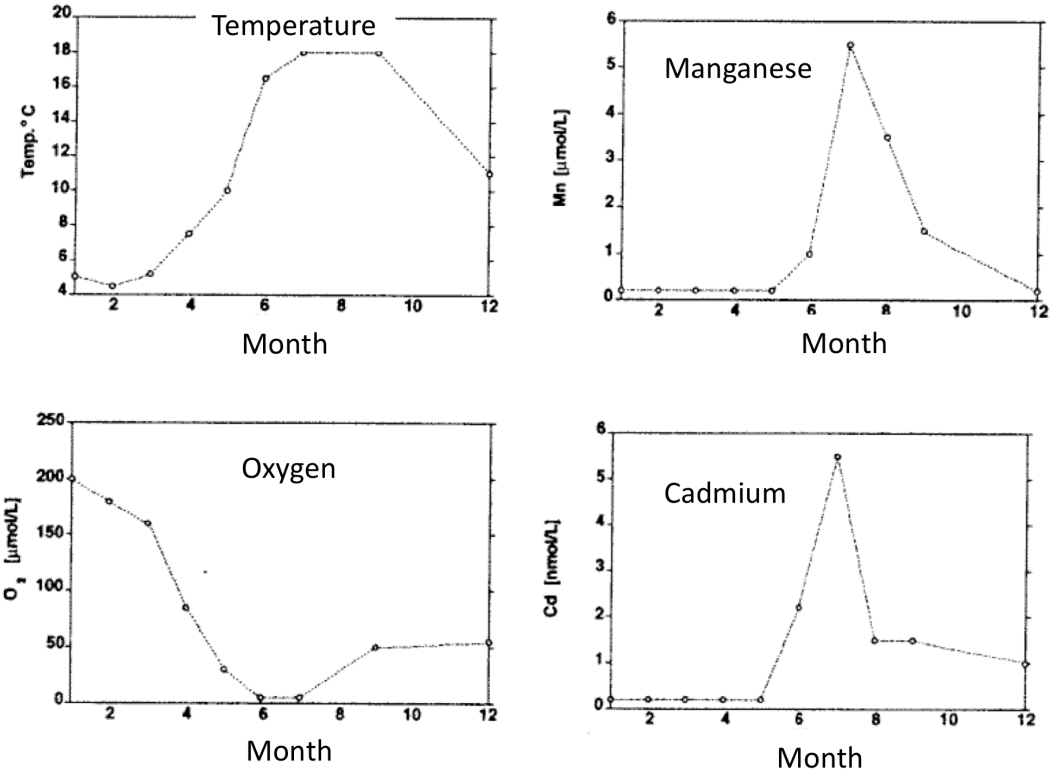
$$pCO_2 = \frac{[HCO_3^-][H^+]}{K_1 K_H}$$

At 250 m this results in pCO_2 of 0.006 atm which is about 16 times the partial pressure of CO_2 in the atmosphere (0.00038 atm).
If this water is pumped out of the ground, CO_2 will be released which leads to an increase in the pH and a precipitation of $CaCO_3$. To avoid precipitation of $CaCO_3$ in the pipes, this water has to be equilibrated with the atmosphere before it is pumped into the distribution system.

d) Riverbank filtration is an important source for drinking water in Switzerland (ca. 25%). If one considers an oxygen concentration of 8 mg/L (0.25 mM), what is the critical concentration of DOC to yield anaerobic conditions (assumption: DOC present as CH_2O and only source of carbon in the water)?
The consumption of oxygen by CH_2O is a stoichiometric process. Therefore, 1 mol of CH_2O leads to the consumption of 1 mole of oxygen:
Maximum CH_2O (C) concentration: 0.25 mM. This corresponds to 0.25×12 mM C = 3 mg/L C.

e) What happens if the DOC concentration is 5 mg C/L and nitrate is 5 mg/L (assumption: all DOC is biodegradable)?
2 mg/L of the DOC will remain after aerobic respiration (see 2c).
5/4 mol CH_2O will be used up per mol of NO_3^-. This corresponds to 0.13 mM or a maximum of 8 mg/L NO_3^-. Therefore, not all carbon will be utilized which can lead to a reductive dissolution of iron and manganese oxides.

Biogeochemical processes and geochemical consequences
During infiltration of the Glatt river (Glattfelden) samples were taken at one sampling well to obtain seasonal information (month) on temperature, oxygen, manganese and cadmium (Figure below).
f) How do you interpret these field observations?
The temperature in the groundwater follows the seasonal trend of the river water. The oxygen concentration shows the mirror image of the temperature. Even though the solubility of oxygen decreases with increasing temperature, this large effect cannot be explained by solubility alone. Aerobic respiration is the main cause for oxygen loss in this infiltration system.
Manganese increases when oxygen is depleted. This can be explained by reductive dissolution of manganese oxide, leading to dissolved Mn(II).
Cadmium follows a similar trend as manganese(II). Cadmium is not redox active, however, it is released together with manganese. This points towards a release of Cd which is adsorbed to the surface of manganese oxides.
g) What parameters are problematic from a point of view of drinking water?
Manganese: The maximum manganese concentration is 5.5 µM which corresponds to 0.3 mg/L. This is above the drinking water standard of 0.05 mg/L.
Cadmium: The maximum cadmium concentration is 5.5 nM which corresponds to 0.6 µg/L. This is significantly below the drinking water standard of 5 µg/L.



3. Phosphate fertilization in a lake

A stagnant lake has a phosphate concentration of 50 µg P/L in the epilimnion. 90% of this phosphate is transformed into biomass which sinks to the hypolimnion. The volume of the epilimnion is 2.5×10^{6} m^3.

a) What is the minimum volume of the hypolimnion to avoid anoxic conditions.

Assumption: the hypolimnion is a completely mixed reactor with an average oxygen concentration of 8 mg/L.

Epilimnion:

Phosphate: 50 µg/L corresponds to 1.6×10^{-6} M, 90% is transformed into biomass: 1.45×10^{-6} M.

Volume of epilimnion: 2.5×10^{6} m^3 = 2.5×10^{9} L

Total amount of P in this volume: 2.5×10^{9} L × 1.45×10^{-6} M = 3.6×10^{3} mol.

Hypolimnion:

Oxygen: 8 mg/L = 2.5×10^{-4} M

1 P consumes 138 O_2, required amount of oxygen: 138 × 3.6×10^{3} mol.

Required volume of hypolimnion: $V = (138 \times 3.6 \times 10^{3})/(2.5 \times 10^{-4}) = 1.99 \times 10^{9}$ L = 1.99×10^{6} m^3.

b) What happens if the volume is smaller and what are the consequences for water quality?

Other electron acceptors will be utilized. If nitrate is fully depleted, iron and manganese oxides will be reductively dissolved, resulting in Mn(II) and Fe(II) which have to be removed for drinking water purposes. Sulfate reduction may lead to sulfide formation which is undesired due to taste and odor problems.

c) An industrial company would like to use lake water for cooling purposes. This is not authorized in Switzerland. Why?

The company would have to take cold water from the hypolimnion. Once it has been used, it would be pumped into the epilimnion again. Since the water from the hypolimnion contains phosphorus, this leads to an internal recycling and an enhanced fertilization of the lake.