

Lake Constance Water Supply: Water Analysis

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Lake Constance Water Supply

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Abstract

In Germany it is common to use tap water for drinking and cooking purposes. People put trust in its quality thanks to the high-level treatment facilities in our country.

But is the water really clean or is it affected by the water pipeline system?

In this project the students will analyze the quality of the water supplied in Stuttgart in Southwest Germany and compare it to the original water from its source at Lake Constance in South Germany. We want to follow the steps taken to treat lake water with its source in the Alps to drinking water quality level and how treatment plants in Germany, especially in Baden-Württemberg, operate.

Consequently we look into what criteria are applied to control drinking water quality and if the quality is impacted on a chemical level by the transport within the pipeline system.

1 Introduction

1.1 General Situation

The “**Bodensee-Wasserversorgung**” (BWV, eng.= Lake Constance Water Supply) was founded as a non-profit organization on the 25th of October 1954 in order to supply the Metropolitan Area of Stuttgart and surrounding regions with drinking water. Today it is one of the largest long distance water supply systems in Germany and delivers water to approximately 4 million people in 320 cities and communities. About 130 million m³ of water are supplied to the customers per year. This is around one percent of the total influx of the Lake Constance and much less than the water, which is lost by evaporation at the surface of Lake Constance. The underground tubing system has a length of 1,700 km and contains 29 covered reservoirs with a total volume of 470,600 m³.

The water intake is 60 m below the surface of Lake Constance. The water is pumped into the swelling pot and after that flows due to gravity to the micro strainers to remove organic materials, which is then followed by an ozonisation. After ozonisation the water is filtered by layers of 40 cm anthracite coal and 60 cm fine quartz sand on a 60 cm wide supporting layer of gravel.

Low amounts of iron salt (FeCl₃) are added to ease the precipitation. After filtering, the water flows into the reservoir and very low amounts of chlorine dioxide are added to inhibit bacterial growth.

Other information see 6.1 [5,6].

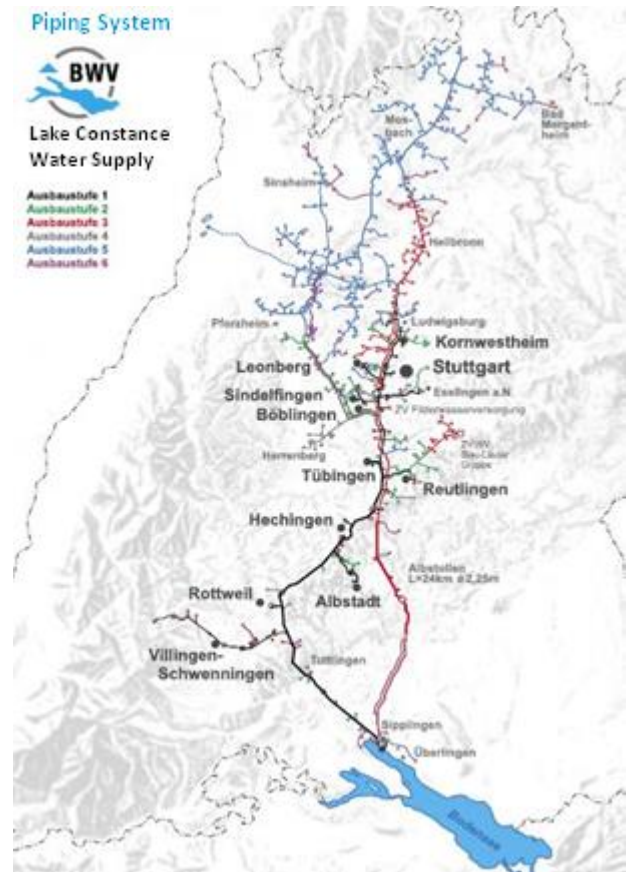


Figure 1: Piping system of the Lake Constance Water Supply

In the water supply system in Baden-Württemberg the drinking water in the first main pipe flows passively (downwards) from the treatment plant to the Metropolitan Area of Stuttgart (red pipe/pipe on the right side).

The drinking water in the second main pipe (black pipe/pipe on the left side) is pumped upwards to the area of Tuttlingen. After that the drinking water flows passively to the Metropolitan Area of Stuttgart.



Figure 2: Swelling pot at the treatment plant of the Lake Constance Water Supply (BWV)

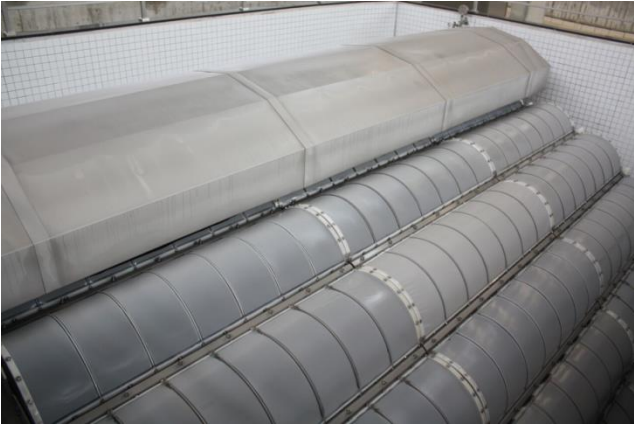


Figure 3: Micro strainers at the BWV

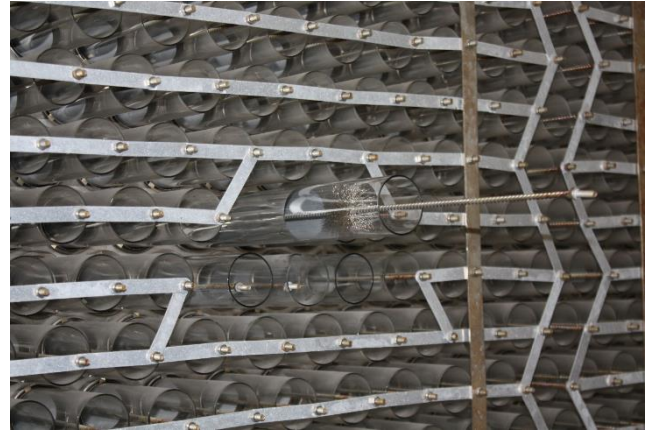


Figure 6: Inside the ozonisation chamber at the BWV

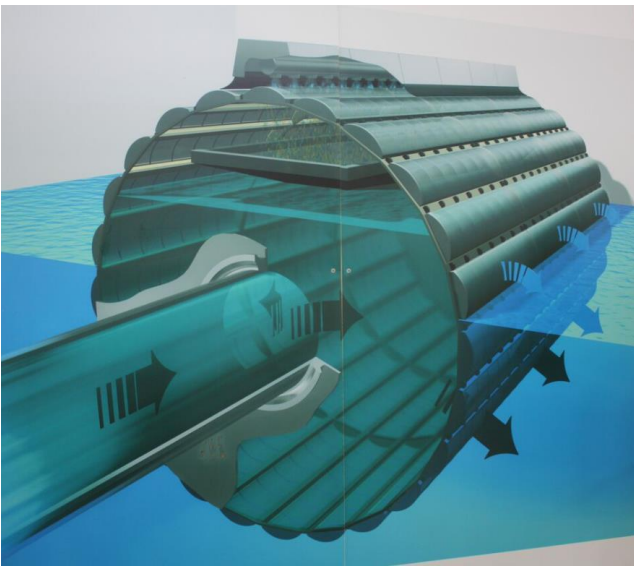


Figure 4: Schematic procedure of the micro strainers at the BWV

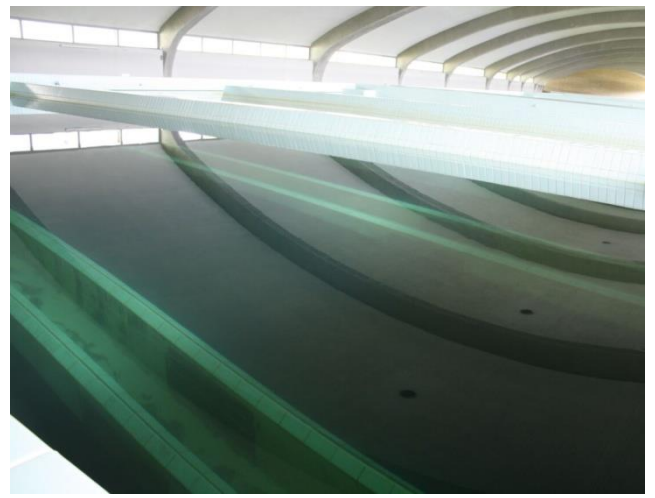


Figure 7: Filter with different layers at the BWV (view from the top)



Figure 5: Ozonisation chambers at the BWV



Figure 8: Filter with different layers (profile view)

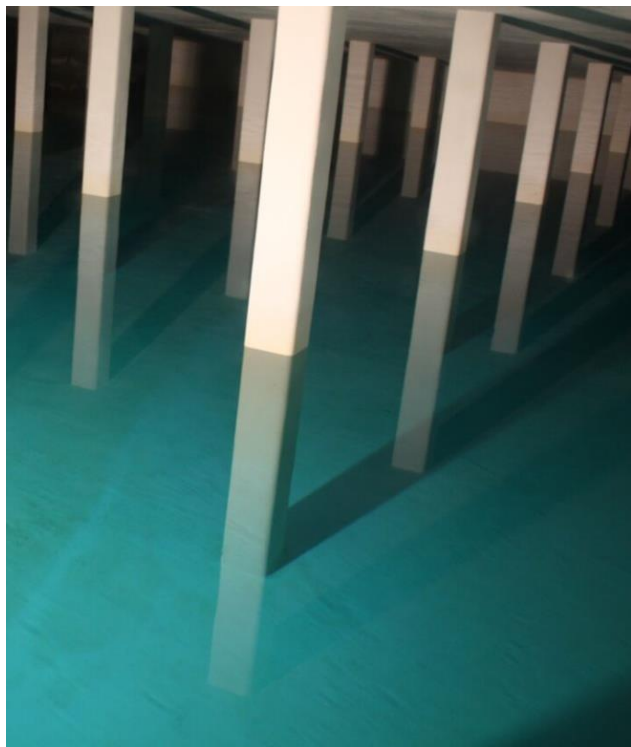


Figure 9: water reservoir at the BWV



Figure 10: Aerial view of the water treatment plant in Sipplingen on top of a mountain (Sipplinger Berg). Lake Constance with the water intake is on the right side.

The aim of this project is to analyze water from the surface of Lake Constance before and after the treatment at the plant in Sipplingen and from the tap drawn in Stuttgart for several constituents by analytical chemical tests. The results of these tests are compared to the water analysis published by BWV and compared to the legal maximum limits according to the *Deutsche Trinkwasserverordnung* TVO, (German Drinking/ Tap Water Ordinance). As an outlook we discuss the risk of other chemical substances occurring in water obtained from long distance water supply systems.

2 Methodology

2.1 Chemical Analysis

2.1.1 Material

Water was obtained in Sipplingen, Lake Constance, from the lake surface, at the water treatment plant at the water intake, and at the tap in Stuttgart. Sampling followed standard procedures from selected outlets (flushing of 2L, collection in borosilicate bottles with Teflon closures, storage at 10°C until analysis). Analysis was performed with MColortest #1.11151.0001 Merck Millipore, Darm-

stadt, Germany, according to the manufacturer's instructions.

2.1.2 pH value:

The pH value specifies the acidity or basicity of a solution. The pH value has no unit.

$$\text{pH} \approx -\log(c(\text{H}_3\text{O}^+))$$

$$c(\text{H}_3\text{O}^+) \approx 10^{-\text{pH}}$$

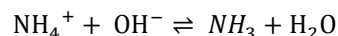
The pH value can be measured with the help of the universal indicator, which is a composition of different indicators with different colors for corresponding acids and bases. Therefore, due to the chemical balance and the law of mass action, the solution changes its color when the concentration of hydronium ions in the solution changes. Every concentration (between pH 1 and 14) has its own color, which makes it rather easy to determine the pH value through colorimetric measurement.

Measuring range: 1- 14

2.1.3 Concentration of ammonium ions:

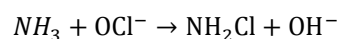
The concentration of ammonium ions in water (if there is no extra ammonia in the air except the ammonia which forms through the chemical balance of ammonia and ammonium ions dissolved water) can be determined colorimetric with the help of the Berthelot's reaction. The Berthelot's reaction consists of the following reactions:

The ammonium ions dissolved in water are in a chemical balance with ammonia in the air:



At a pH value of about 13, almost all/all ammonium ions have reacted to ammonia, which is why the concentration of the ammonium ions can be determined through further reactions with only ammonia.

In combination with hypochlorite the ammonia molecules react to hydroxide and monochloramine:



In combination with thymol ($\text{C}_{10}\text{H}_{14}\text{O}$) in the basic/alkaline solution/medium the monochloramine first reacts to N-chlor-2-isopropyl-5-methyl chinon-monoimin with the 1st thymol molecule and further to correspondent indophenol molecule with a 2nd thymol molecule.

1st reaction:

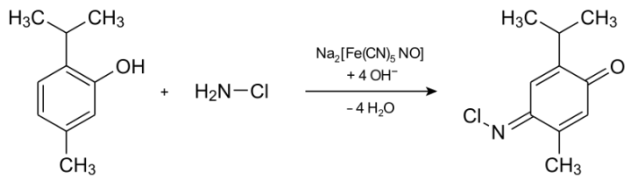
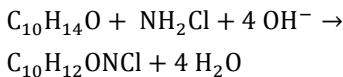


Figure 11: Reaction of thymol and monochloramine in an alkaline medium

2nd reaction:

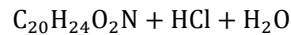
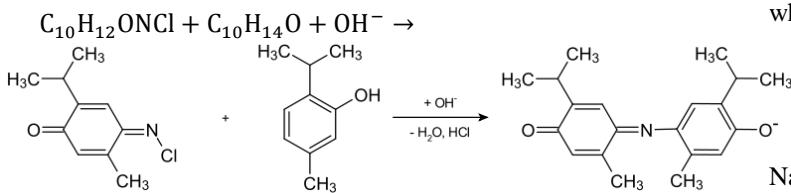
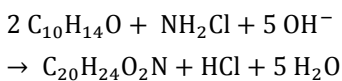


Figure 12: Reaction to indophenol

Condensed reaction:



The indophenol molecule is in basic/alkaline solution absorbing orange light, making absorbed white light blue.

The higher the concentration of the ammonium ions was, the higher is the concentration of the indophenol molecules, which makes the solution appear in a darker shade of blue. With the help of a color scale and therefore through colorimetric determination the concentration of the ammonium ions in the water can be determined.

If there is extra ammonia in the air, which didn't form through reaction of hydroxide ions, the maximum concentration of ammonium ions possible (in the case of all ammonia being dissolved in water) is determined. Due to this the concentration, which is determined with the help of Berthelot's reaction, is called total ammonium concentration.

The unit used for describing the total ammonium concentration is mg/L.

Measuring range: 0- 5 mg/L

2.1.4 Total hardness:

Expresses the hardness of the water, which is due to the hardening constituents. They are the salts of the alkaline earth metals calcium, magnesium, strontium and barium. Because there are only very small traces of strontium and barium ions dissolved in water, the determination of the total hardness is reduced to only magnesium and calcium. Furthermore, in conventional determinations the total

hardness is defined as the concentration of calcium ions in the water, expressing also the portion of magnesium. The percentage of magnesium is then given separately to the concentration, making it possible to separately calculate the concentrations of calcium and magnesium ions in the water.

The units used to describe the total hardness are the English degree (°e), the German degree (°d), mg/L CaCO₃ and the formally and internationally used unit mmol/L Ca²⁺.

The concentration of Mg²⁺ and Ca²⁺ is determined through a titration with ethylenediaminetetraacetic acid disodium salt dehydrate (Na₂EDTA / Na₂C₁₀H₁₄N₂O₈) and the help of an indicator called eriochrome black T (C₂₀H₁₂N₃NaO₇S) in mixture with methyl orange, which serves as a colorant.

The indicator binds with a portion of magnesium and calcium ions dissolved in water. This creates a complex which lets the solution appear in red. That's due to eriochrome black T's characteristic of absorbing yellow light in a complexes with Ca²⁺ or Mg²⁺, letting the complexes appear purple. Furthermore the mixture with methyl orange makes the solution appear red.

Na₂EDTA binds with the ions of the alkaline earth metals dissolved in water first. After that the Na₂EDTA binds with the alkaline earth metals in the complex with eriochrome black T, setting the indicator free. Setting the indicator free makes the solution appear green or greenish. That is due to eriochrome black T's characteristic of absorbing purple light in alkaline mediums, which lets eriochrome black T appear yellow. In mixture with methyl orange the solution appears green.

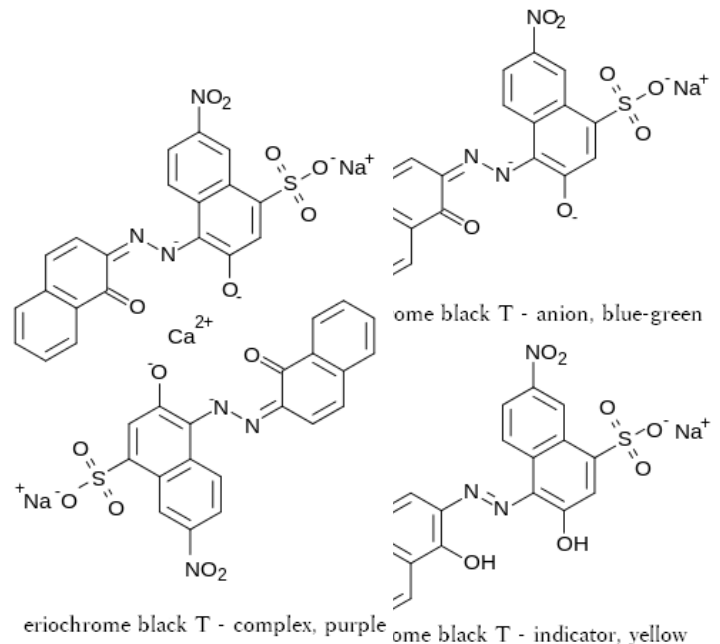


Figure 4: Eriochrome black T anion, indicator and complex

2.1.5 Carbonate hardness / acid-binding capacity:

Carbonate hardness is the concentration of Ca²⁺ and Mg²⁺ ions with an equivalent quantity of hydrogen carbonate ions (HCO₃⁻) and carbonate ions (CO₃²⁻). If the quantity of hydrogen carbonate ions and carbonate ions is higher than the total hardness, carbonate hardness is the total hardness, because there are enough hydrogen carbonate and carbonate ions for the calcium and magnesium ions.

Consequently the units for carbonate hardness are (like for the total hardness) the German degree ($^{\circ}d$), the English degree ($^{\circ}e$) and mmol/L Ca^{2+} .

Due to hydrogen carbonate and carbonates capability of binding acids, carbonate hardness can be expressed through the acid binding capacity (ANC). But because carbonate ions and hydrogen carbonate ions can bind twice as much acid as Ca^{2+} and Mg^{2+} (due to the bivalency of calcium and magnesium ions) the ANC is higher in comparison with the total hardness by a factor of 2. The unit used to describe the ANC is mmol/L.

Formula for the calculation of ANC in carbonate hardness:

$$\frac{ANC(mmol/L)}{2} = \text{carbonate hardness (mmol/L)}$$

The acid binding capacity is defined as the quantity of hydrochloride ($c=0.1$ mol/L) which is required to titrate a sample of water with the volume of 100ml to a pH value of 4.3. At a pH of 4.3 the ANC is saturated, therefore all carbonate and hydrogen carbonate ions have taken up the protons given through hydrogen chloride.

Due to the similar units of total hardness and carbonate hardness, the last 3 formulas apply on both total and carbonate hardness.

$$ANC \left(\frac{mmol}{L} \right) \times 2.8 = \text{German degree } (^{\circ}d) = \text{carbonate hardness} \left(\frac{mmol}{L} \right) \times 5.6$$

$$ANC \left(\frac{mmol}{L} \right) \times 3.5 = \text{English degree } (^{\circ}e) = \text{carbonate hardness} \left(\frac{mmol}{L} \right) \times 7$$

$$\text{German degree } (^{\circ}d) \times 1.25 = \text{English degree } (^{\circ}e)$$

$$\text{German degree } (^{\circ}d) \times 0.178 = \frac{mmol Ca^{2+}}{L}$$

$$\text{German degree } (^{\circ}d) \times 17.85 = \frac{mg CaCO_3}{L}$$

Measuring range for both total hardness and carbonate hardness: 0.2(0.5) - 20 $^{\circ}d$

2.1.6 Nitrate (NO_3^-) concentration:

Nitrate is reduced to nitrite and reacts with sulfanilic acid to form a diazonium salt. This in turn reacts with 2,5-dihydroxybenzoic acid to form an orange-yellow azo dye, which is then determined colorimetrically.

Measuring range: 0- 150 mg/l

2.1.7 Nitrite (NO_2^-) concentration:

Nitrite reacts with sulfanilic acid to form a diazonium salt, which in turn reacts with N-(1-naphthyl)ethylenediamine dihydrochloride to form a red-violet azo dye (Griess test). This is then determined colorimetrically.

Measuring range: 0- 0.5 mg/l

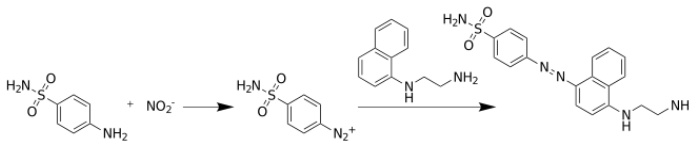


Figure 13: Reaction of Nitrite with sulfanilic acid.

2.1.8 Phosphate (PO_4^{3-}) (orthophosphate) concentration:

Orthophosphate ions react with molybdate ions to form molybdophosphoric acid. This is in turn reduced to phosphomolybdenum blue (PMB), which is then determined colorimetric.

Measuring range: 0- 3.0 mg/l

2.1.9 Oxygen (O_2) concentration:

Oxygen oxidizes bivalent manganese to higher-valence manganese hydroxides. In the subsequent reduction with iodide to Mn(II), a quantity of iodine equivalent to the dissolved oxygen is formed, with the solution changing from violet to blue in color, depending on the oxygen content, in the presence of starch as indicator. The iodine is then titrated with sodium thiosulfate until decoloration of the solution. The reduction of the oxygen content of water caused by oxygen-consuming chemical and biochemical processes is generally referred to as oxygen consumption. When the oxygen depletion is due to microorganisms and the measurement is performed under defined conditions, this process is also referred to as biochemical oxygen demand or BOD. The BOD is defined as that amount of oxygen that is consumed by microorganisms in n days to oxidatively degrade the organic substances present in one liter of water at a temperature of 20 $^{\circ}C$. The BOD provides a point of reference for the assessment of water regarding its load with biologically oxidizable organic substances and its biological activity. The reason why the BOD is not determined until after one or more days is because biological processes take considerably more time than chemical processes. In most cases organic substances have been biologically degraded to a degree of approximately 70% after five days ($n=5$). Therefore, the BOD is generally determined after this period of time (BOD5).

Measuring range: 0.1-10mg/L

For information concerning the expected chemical analysis of the water samples and the legal limits see 6.1.[8]. For surface water no legal limits exists for water without specified use (i.e. not for drinking).

2.2 Microbiological analysis

Microbiological analysis could not be performed because of legal restrictions in Germany concerning microbiological testing by (underage) students.

3 Results

The water samples are abbreviated as follows:

Surface water/ Epilimnion: **SW**

Raw water/ unspiked water/ untreated water (from 60 m below water surface): **RW**

Treated water (from the 1st main pipe at the treatment plant): **TW**

Tap water from Stuttgart: **W**

3.1 Chemical Analysis

3.1.1 pH value:

Table 1: pH value of the four water samples

	SW	RW	TW	W
pH value	≈ 8	≈ 8	≈ 8	≈ 8
Expected value	7,63	7.99	7.99	8.02

3.1.2 Concentration of ammonium ions:

Table 2: Ammonium ion concentration of the four water samples

	SW	RW	TW	W
Concentration - Ammonium (in $\frac{mg}{L}$)	≈ 1.5	< 0.1	≈ 0	< 0.1
Expected value (in $\frac{mg}{L}$)	0.58	< 0.01	< 0.01	< 0.05

3.1.3 Total hardness:

Table 3: Total hardness of the four water samples

Total hardness	SW	RW	TW	W
in °d	10	10	9.5	10
in $\frac{mmol Ca^{2+}}{L}$	1.78	1.78	1.69	1.78
Expected values				
in °d	9	9	9	9.1
in $\frac{mmol Ca^{2+}}{L}$	1.60	1.60	1.60	1.62

3.1.4 Carbonate hardness:

Table 4: C hardness of the four water samples

Carbonate hardness	SW	RW	TW	W
in $\frac{mmol}{L}$	1.65	1.65	1.25	1.35
SNC (in $\frac{mmol}{L}$)	3.3	3.3	2.5	2.7
Expected values				
in $\frac{mmol}{L}$	1.26	1.275	1.275	1.25
SNC (in $\frac{mmol}{L}$)	2.52	2.55	2.55	2.5

3.1.5 Concentration of Nitrate:

Table 5: Nitrate concentration of the four water samples

	SW	RW	TW	W
Concentration - Nitrate (in $\frac{mg}{L}$)	≈ 2	0	0	0
Expected value	4.5		4.2	4.2

(in $\frac{mg}{L}$)

- For RW and TW (if not stated specifically otherwise) - see 6.1.[3]
- For W - see 6.1.[4]

3.1.6 Concentration of Nitrite:

Table 6: Nitrite concentration of the four water samples

	SW	RW	TW	W
Concentration - Nitrite (in $\frac{mg}{L}$)	0	0	0	0
Expected value (in $\frac{mg}{L}$)	–	–	< 0,005	< 0.005

3.1.7 Concentration of Phosphate:

Table 7: Phosphate concentration of the four water samples

	SW	RW	TW	W
Concentration - Phosphate (in $\frac{mg}{L}$)	0	0	0	0
Expected value (in $\frac{mg}{L}$)	–	–	< 0.003	< 0.003

3.1.8 Concentration of Oxygen:

Table 8: Oxygen concentration of the four water samples

	SW	RW	TW	W
Concentration - Oxygen (in $\frac{mg}{L}$)	6.5	6.5	7.1	7
Expected value (in $\frac{mg}{L}$)	–	–	16.9	16.9

Expected values (all tables):

- For SW - see 6.1.[1,2]

4 Conclusion

4.1 Conclusions for the specific parameters

4.1.1 pH value:

No greater changes in the pH value were detectable, therefore no greater quantity of acids or bases could have been dissolved in the water during the transportation from Lake Constance to Stuttgart.

4.1.2 Concentration of Ammonium ions:

There was a greater change in the concentration of ammonium between the surface water and the other water samples.

The difference could be originating from separated layers of water in Lake Constance. The upper layer is warmer most of the time in a year, which naturally separates it from the deeper and colder water layer. There is almost no mass transfer between these two layers of water, due to the differing densities of the two water layers. Only in winter (approximately between December and March) there is a mass transfer due to the decrease in temperature and therefore increase of density of the upper layer.

Because there is almost no mass transfer, because the winter this year in Germany wasn't that cold, the time in which there was mass transfer has been shorter than usually. Due to this there was no balancing of ammonium concentration since the end of March. A reason of the decreased concentration in the deeper layers could be the use of ammonium ions as food for living organisms in this water layer. The increased concentration of ammonium ions in the upper layer is probably originates from fertilizers (like Ammonium chloride (NH_4Cl) or liquid manure), which dissolve in water and are then transported through rivers into Lake Constance.

4.1.3 Total hardness:

There were no greater fluctuations in the concentration of calcium and magnesium ions between Lake Constance and Stuttgart.

This means that calcium and magnesium ions were neither inserted nor extracted from the water during the transport of the water to Stuttgart.

4.1.4 Carbonate hardness:

There were slight fluctuations in carbonate hardness, although, according to official sources, there shouldn't be.

A reason for the fluctuations in carbonate hardness could be errors or inaccuracies in the determination of the carbonate hardness.

Otherwise there is the possibility of CO_2 dissolving in water at pumping stations or during sample drawing. The fluctuations could also arise from other metal carbonates than calcium and magnesium carbonate (calcium and magnesium carbonate dissolved in water would change the total hardness, which is not the case) dissolving in water.

4.1.5 Nitrate (NO₃⁻) concentration:

Nitrate was found in higher concentration in the surface water, but was below the limit of detection in the other samples. Like ammonia, nitrate is used as a fertilizer in agriculture. Nitrate and ammonia are predominantly in surface water. The water intake of the Lake Constance Water Supply is at a depth of 60 meters and thus avoids the uptake of these unwanted substances.

4.1.6 Nitrite (NO₂⁻) concentration:

Nitrite could not be found in any of the examined samples.

This is an expected outcome because of the low level of nitrate and ammonia in the examined water samples (ammonia is oxidized to nitrite and nitrate is reduced to nitrite).

4.1.7 Phosphate (PO₄³⁻) (orthophosphate) concentration:

Phosphate was also below the limit of detection. This shows the very effective removal of phosphates used in detergents by the water sewage treatment plants. This diminishes algal growth and as a consequence leads to low number of fish in the Lake Constance. In the water sample taken from the surface of Lake Constance algae was visible to the naked eye.

4.1.8 Oxygen (O₂) concentration:

The concentration of oxygen in our water samples was rather low. The expected concentration was twice as high as the determined values.

4.2 Error Analysis

4.2.1 Titrations:

Titrations are always error-prone, due to the fast change of color, pH or other parameters at the end point of reaction.

Combined with the fact that the used materials have big gradations (up to 0.5°d or 0.25 mmol/L (SNC) per drop), it is highly probable that some of the determined values are too high by 0.5-1°d or 0.25-0.5 mmol/L (SNC).

4.2.2 Colorimetric determination:

Due to different perceptions of color of every person, the colorimetric determined values can differ from the real values.

4.2.3 Oxygen (O₂) concentration:

Prolonged storage of the samples can result in divergent measurements due to a loss of oxygen through the wall of the bottles.

5 Outlook

5.1 Tar pipes

At the beginning of the construction of the Lake Constance

Water Supply, tar was used as building material for the water pipes. Soon the administration union/special-purpose association realized that tar residues dissolved in water are quite unhealthy. Therefore the tar pipes have been removed.

But have all tar pipes really been removed or are there still some tar pipes left, due to for example false records or false information from the construction site?

A possible solution would be a specific search for and renewal/exchange of tar pipes in the piping system. A narrowing of the search range could be achieved by examining water samples in the search range.

5.2 Corrosion in water pipes

The second type of water pipes which were used for construction is a composition of two layers. The first layer (the layer directly exposed to water) is built up out of a material which is impermeable to water, namely cement and/or bitumen. The second layer (the layer providing the main stability) is made of steel or cast iron.

Due to, for example, construction works and other external influences, there is the possibility of the water pipes being damaged. If the first layer is damaged and the second layer is not protected and therefore exposed to the water, (heavy) metals can dissolve in the water which has negative effects on the health of a person who drinks this water.

A possible solution would be a search for and renewal of the bitumen-iron/-steel pipes with the same strategy as described in 5.1.

Corrosion of iron is only of low concern since iron does precipitate and would lead to a rusty look of the water and therefore early complaints by the customers. Furthermore there is a high probability that possible scratches in the surface of the pipes, which could lead to corrosion, would be closed by precipitated deposits in the damaged zones.

For a search for these obsolete tubing systems, very sensitive analytical systems have to be employed. In general, photometric tests such as those used for our testing are not appropriate. More sensitive techniques such as gas chromatography – mass spectrometry (GC-MS) have to be employed instead.

5.3 Corrosion at home

Corrosion is not bound to the piping system of the Lake Constance Water Supply, it can also occur in the piping system at home. Especially in old houses corrosion can occur, due to older pipes (therefore more time for erosion) and other materials of the pipes.

A possibility to identify whether or not the pipes of the house are the pipes of concern is the examination of multiple tap water samples from different houses in one area. If the water pipes of the Lake Constance Water Supply are damaged, all samples have signs of the corrosion (higher concentration of dissolved metals). If the pipes of one/a few houses are rusty, only a few samples will have a higher concentration of metals in it.

However, corrosion of water pipes is only of low importance since lead pipes were abandoned in 1878 in Swabia. Corrosion might occur particularly in zinc-coated tubes. The larger diameters used in these tubes lead to

lower flow rates and as well as a rather thick deposition of limestone and iron covers the inner surface of the tubes.

For the testing of corrosion, water testing in particular for lead, zinc and copper should be done. These tests are normally done by atomic absorption spectroscopy (AAS).

5.4 Constant contamination of tap water

The Lake Constance Water Supply started working in 1958. At that time the oldest pipes in the piping system were just about 1 year old. Today these pipes, which are only a small part of the whole piping system, are more than 60 years old. With an expected lifespan of 100 years the first pipes are already being renewed to make sure that all pipes are switched before the lifespan of each pipe ends.

But due to these renewals and other construction, the water may be contaminated by dust, dirt and construction debris.

One solution could be to let the water up to a defined point before the construction site and the redirection of the water through one of the many other pipes to another point after the construction (→ water comes from the opposite direction to the specific point after the construction site). One downside would be the energy for the water pumps for the transportation of the water back into the direction of Lake Constance. Most of the pipes are tilted downwards (seen in the direction of the regular flow of the water), which is the reason why energy would be needed to transport the water in the opposite direction.

6 Summary

Our analyses showed that the design of the long distance water supply system with the water intake far below the surface of Lake Constance avoids the contamination of the drinking water by anthropogenic and agricultural chemicals, in particular nitrate and ammonia. All tests performed showed concentrations of the chemicals well below the limits of TVO and with (almost) no differences between the different collection points. We can conclude that neither by the treatment nor by the transport of the water through the long tubing systems these chemical parameters are changed and that the water obtained at the tap is safe in regard of these parameters.

However, contamination of drinking water can also occur by adulteration (e.g. by terroristic attacks or acts or ransom) or by substances used for the tubing system. Adulteration is minimized by the undisclosed place of water intake and the depth of the intake. The intake of unwanted chemicals is regulated by the state-of-the art technologies in particular for the inner surface of the tubing, the material of the gaskets used in the tubing system and the lubricants used during the process of connecting the tubing system.

7 References

7.1 Information and Facts

- [1] <http://www.stadtwerk-am-see.de/pdf/privatkunden/wasseranalyse-hoedingen.pdf>
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7.2 Figures

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- [2] Photograph taken on April 6, 2016
- [3] Photograph taken on April 6, 2016
- [4] Photograph taken on April 6, 2016
- [5] Photograph taken on April 6, 2016
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