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# **Groundwater Chemistry and Treatment: Application to Danish Waterworks**

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Additional information is available at the end of the chapter

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## **1. Introduction**

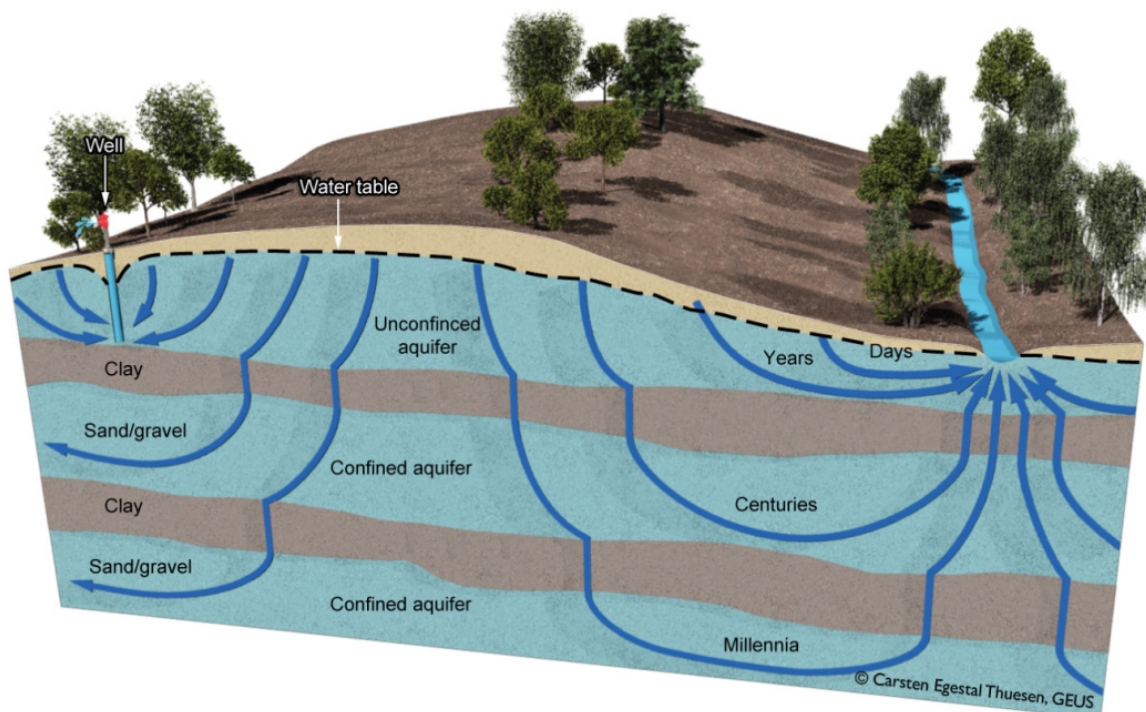
Groundwater plays a pivotal role in Denmark. It is used for both agricultural and industrial purposes, but most importantly all Danish drinking water is produced from groundwater. To comprehend and discuss the processes and issues involved in the production of drinking water in Denmark, an understanding of the composition and the formation of groundwater is highly important.

## **2. Groundwater formation**

Groundwater is formed by rain infiltrating the soil and subsurface, and as a result, the final composition of the water depends on both the specific geological formations and the residence time of the water in these. With respect to groundwater, the subsurface may be divided into two zones: the unsaturated zone and the saturated zone. In the unsaturated zone, the voids between particles are a mixture of water and air, while in the saturated zone all the voids have been filled with water. The transition from the unsaturated to the saturated zone marks the beginning of the water bearing layers; the groundwater. This is also called the water table.

As water infiltrates the subsurface, it moves from the highest hydraulic head to the lowest. Since land is generally higher elevated than water bodies such as rivers, lakes and the sea, these will usually be the final destination for the water. For a given hydrological area, this is called the discharge area, while the area in which the water infiltrates is called the recharge area. If the recharge area is far from the discharge area, the water will move almost vertically downward until it reaches a confining layer, see Figure 1. From here the water moves horizontally towards the discharge area, until it meets an opposing force that forces it upwards. If the discharge area is a river or a lake, this opposing force may be water coming from other directions, and if the discharge area is the sea, it will be the seawater, which will

force the groundwater upwards due the difference in density. If the recharge area is closer to the discharge area, the path of the water will be more curved. It will not reach the the same depth and will have a considerably shorter residence time. Also, as the water nears the discharge area, the flow of water will increase due to the incompressibility of water.



**Figure 1.** Illustration of groundwater flow and retention times as a function of distance between recharge and discharge area and depth of aquifer. Modified from *Viden om Grundvand* (15).

The movement of groundwater depends on the permeability of the water bearing layers. Layers such as clay have a low permeability and tend to inhibit water flow, whereas sand or chalk layers have a high permeability and promote water flow. In the subsurface, low permeable layers will act as confining beds, while high permeable layers will be water bearing layers. A geological unit from which groundwater may be extracted is called an aquifer, and there may be distinguished between two types: unconfined and confined aquifers. A confined aquifer is a water bearing layer completely enclosed by confining layers. These aquifers will only slowly recharge, but are also well protected against anthropogenic pollution from the surface. An unconfined aquifer is in direct contact with the surface, and will as such rapidly recharge depending on the amount of rainfall, but will also be more exposed to activities on the surface.

In Denmark, the majority of cities are situated near the ocean, and the available aquifers will most often be unconfined and placed close to the surface. If water is extracted from greater depths, it will be salty because the dense seawater forces the fresh groundwater further inland. The groundwater directly underneath the cities will as such be heavily influenced by the activity on the surface, and in recent years it has been found to be polluted with compounds such as chlorinated organic solvents and pesticides originating from industries

and park maintenance (1). Furthermore, because water from the entire recharge area flows past the city on its way to the discharge area, pollution of the water in the recharge area may end up affecting the water quality in the city. Because Denmark is heavily populated and cultivated relative to its size, most recharge areas are farming land. This has led to increasing problems with pesticides and fertilizers used by the farmers, even though these farming chemicals are applied far from the city.

### 3. Groundwater composition

The most important factors affecting the composition of groundwater is the composition of the water after the immediate infiltration of the top layers of the surface, the geology of the subsurface, and the flow rate of the water through the subsurface. As the water moves through the subsurface, it is constantly approaching equilibrium with the surrounding geological layers. The type of equilibrium reactions are determined by the initial composition of the water and the specific geology of the subsurface, which therefore becomes very important for the final composition of the groundwater. The flow rate of the water controls the time available for the water to reach equilibrium with the surroundings, which is important since the equilibrium reactions vary in rate of reaction. In the upper part of the subsurface, the composition of the water is mainly determined by pH and redox conditions, and because of differences in rate of reaction, specific zones and fronts will be formed. These fronts and zones are general, and will be found in most places. At deeper levels, the retention time for the water is greatly increased, and slower reactions become influential. Here the specific geological conditions determine the composition of the groundwater, and this may result in very different types of groundwater. The type of groundwater is defined based on a division of its constituents into a number of groups as seen in Table 1. To understand the presence of these constituents, a more detailed description of the before mentioned processes is necessary.

Group		Constituents
Main components	Cations	$\text{Ca}^{2+}$ , $\text{Na}^+$ , $\text{NH}_4^+$ , $\text{K}^+$ , $\text{Mg}^{2+}$ , $\text{Fe}^{2+}$ , $\text{Mn}^{2+}$
	Anions	$\text{HCO}_3^-$ , $\text{NO}_3^-$ , $\text{SO}_4^{2-}$ , $\text{PO}_4^{3-}$
Uncharged species		$\text{H}_4\text{SiO}_4$
Trace components		$\text{Al}^{3+}$ , $\text{Ni}^{2+}$ , $\text{Zn}^{2+}$ , $\text{F}^-$ , $\text{H}_3\text{AsO}_3$ and others
Gases		$\text{CO}_2$ , $\text{H}_2\text{S}$ , $\text{CH}_4$ , $\text{O}_2$
Organic compounds		Humus
Anthropogenic compounds		Pesticides, chlorinated solvents, and others

**Table 1.** Division of groundwater constituents into component groups.

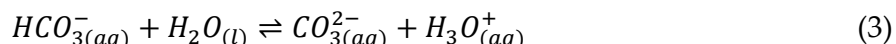
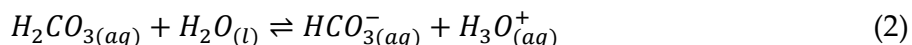
The first factor to influence the groundwater composition is the type of precipitation, which depends on its place of origin. Denmark has a coastal climate, and the rain will as such have a relatively high content of salts compared to rain formed from water evaporated inland. The atmospheric conditions also affect the composition of the rain. Combustion of fossil fuels may result in formation of  $\text{SO}_x$  and  $\text{NO}_x$  gases, which will dissolve in the rain drops

and form sulfuric and nitric acid. Ammonia evaporation from farming industry may also lead to the formation of nitric acid, see equation 5.

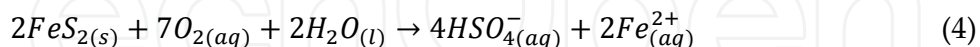
On the surface and in the upper layers of the soil, substances like pesticides, fertilizers and organic solvents may be present due human activity (anthropogenic compounds) together with naturally occurring compounds, and these may dissolve in the water. Which compounds that are present, and how they dissolve in the water depends on the type of land. Different types of land such as forest, farming, or meadow, affects the degree evaporation and biological activity. A high evaporation will result in an increasing concentration of the dissolved compounds, and places with high biological activity may have a large uptake of these compounds and hereby change the composition of the water. The degree of biological activity will also influence the acidity of the water. Besides the anthropogenic acidifiers in the atmosphere, the natural content of  $\text{CO}_2$  in the air will equilibrate with the rain drops, but in places with high biological activity this  $\text{CO}_2$  contribution only plays a minor role. The microbial degradation of organic matter produces concentrations of  $\text{CO}_2$  in the air trapped in the pores, which may be between 10-100 times higher than the concentration in atmospheric air (2). It will as such determine the acidity of the rain to a larger degree than the atmospheric  $\text{CO}_2$ . The acidity of  $\text{CO}_2$  stems from its equilibrium with water, in which it dissolves and forms carbonic acid.



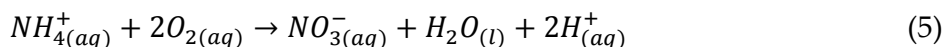
Carbonic acid is a diprotic acid and may convert to either bicarbonate or carbonate depending on pH ( $\text{pK}_{a1} = 6.351$ ,  $\text{pK}_{a2} = 10.329$ ;  $T = 25^\circ\text{C}$ , zero ionic strength (3)).



As the water infiltrates the soil, it will initially contain  $\text{O}_2$  from equilibrium with the atmospheric air, and this promotes redox processes, which may also affect the acidity. In places with pyrite minerals, bisulfate can be formed during the oxidation of the sulfide minerals.



Also, when ammonium is present under oxidizing conditions, it may be oxidized to nitric acid.



As mentioned previously, the content of the water will change progressively as the water infiltrates deeper into the subsurface. For the pH driven processes, the order of reaction is determined by the  $\text{pK}_a$  values of the minerals in the subsurface. For the redox processes, the redox potential is the driving force. In reality pH and redox will often both affect the solubility of minerals, but for the sake of the overview, a distinction is made between important pH and redox driven processes.



## pH driven processes

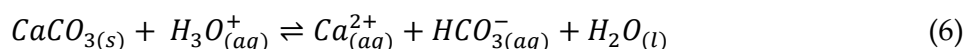
Some of the most important pH driven processes are:

- Dissolution of  $\text{CaCO}_3$
- Dissolution and conversion of silicates
- Ion exchange with  $\text{H}^+$
- Dissolution of hydroxide minerals

The processes are listed in the order they become influential as the pH is lowered.

### *Dissolution of $\text{CaCO}_3$ and hardness*

Because of its basic nature, calcium carbonate is highly affected by pH, and its low solubility makes it one of the main issues in the use of groundwater for drinking water. Calcium carbonate will be in equilibrium with the  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  ions in the water, and as pH is lowered, carbonate ions will convert to bicarbonate and more calcium carbonate dissolves.



Over time, the result is a removal of calcium carbonate, and the longer the surface has been exposed to rainfall the further down into the subsurface, calcium carbonate will have been dissolved. This creates a front, which is known as the acidic front. Below the front, calcium carbonate acts as a buffer, and the pH will be between 7 and 8. Above the acidic front there is no calcium carbonate to neutralize the  $\text{CO}_2$ , and if the water table is above the acidic front, the groundwater here will have a higher content of  $\text{CO}_2$ . Because this may lead to corrosion in drinking water equipment, this type of groundwater is said to contain aggressive  $\text{CO}_2$ .

High concentrations of dissolved calcium carbonate can also be an issue. When groundwater is exposed to the atmosphere or is heated,  $\text{CO}_2$  will diffuse out of the solution, which then becomes supersaturated with calcium carbonate. Groundwater's content of calcium carbonate is commonly given in units of hardness, which is actually a measure of the content of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions in the water. Magnesium is included since it is often found along with calcium minerals and has similar characteristics. Hardness is divided into three types: Total, transient and permanent. The total hardness is the total sum of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions. The transient hardness is the amount of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions dissolved as a result of  $\text{CO}_2$ .

Hardness classification	Total hardness °dH	$\text{Ca}^{2+} + \text{Mg}^{2+}$ meq/L	$\text{Ca}^{2+}$ mg/L *
Very soft	0-4	0 - 1.4	0 – 2.0
Soft	4-8	1.4 - 2.8	28 – 56
Medium hard	8-18	2.8 - 6.4	56 – 128
Hard	18-30	6.4 - 11	128 – 220
Very hard	>30	>11	> 200

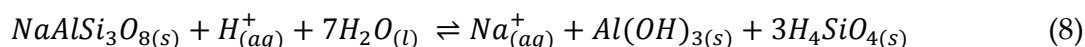
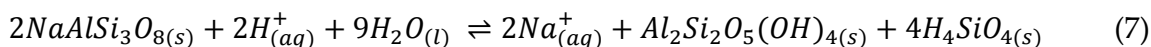
\*The conversion from meq/L depends on the molar mass, and the calcium concentration in the last column has been calculated by assuming that only calcium is present.

**Table 2.** Hardness classification as a function of total hardness (2).

When  $\text{CO}_2$  is driven from the water, this is the amount of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions that will precipitate out of solution. The permanent hardness is the difference between total and transient hardness, and is caused by  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  dissolved by other acids than carbonic acid or  $\text{CO}_2$ . In cases where the concentration of  $\text{HCO}_3^-$  is greater than the content of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions, the permanent hardness is zero. Hardness, in German units  $^\circ\text{dH}$ , is calculated by converting the concentration of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions from mg/L to meq/L and multiplying by 2.8. The typical classification of hardness is given in Table 2.

#### *Dissolution and conversion of silicates*

As pH drops below 6.7, silicate minerals become unstable and start to convert to clay minerals or hydroxides under loss of cations such as  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  and silicic acid. The reactions are complex and slower than the dissolution of calcium carbonate. Examples are given below (4).

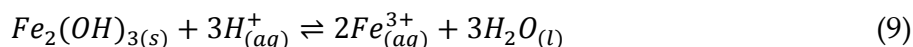


#### *Ion exchange of $\text{H}^+$*

As pH decreases, the adsorption equilibrium of the of  $\text{H}^+$  ions/cations will result in especially  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Ca}^{2+}$  ions being released as  $\text{H}^+$  adsorbs to the minerals. The process becomes more pronounced as the concentration of oxonium increases.

#### *Dissolution of hydroxide minerals*

As the pH drops below 5, hydroxide minerals, most commonly iron and aluminum hydroxides, become partly unstable and start to dissolve.



Because the solubility of iron and aluminum minerals is highly dependent on the oxidation state as well, these processes will also be affected by the redox conditions.

### **Redox driven processes**

The most important processes that are influenced by the redox conditions are:

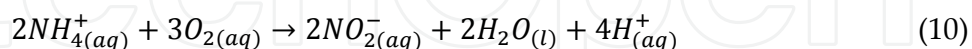
- Nitrification
- Denitrification/sulfide oxidation
- Sulfate reduction
- Methane formation.

All of these are caused by microbes seeking to extract energy from the environment, and they will use the oxidizing agent that produces the largest gain in energy. The available oxidizing agents in groundwater are oxygen, nitrate and sulfate, listed in order of falling redox potential. As a result, the redox processes occurs in different zones. Near the surface, oxygen from the atmosphere is present in the water, and the redox conditions are oxidizing.

As the oxygen becomes depleted, the microorganisms start using nitrate if present, and redox conditions become weakly reducing. The transition from the oxidizing  $O_2/NO_3^-$  environment to the reducing  $NO_3^-$  environment is often called the nitrate front and the anoxic zone.

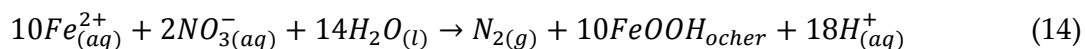
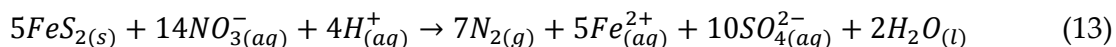
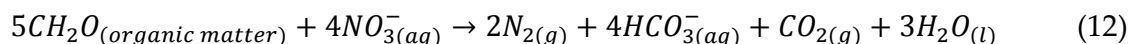
### *Nitrification*

In the nitrification process, ammonium is oxidized to nitrite, which is further oxidized to nitrate.



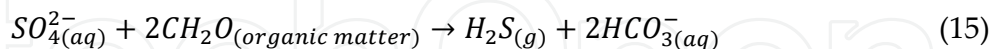
### *Denitrification and sulfide oxidation*

Under anaerobic conditions, nitrate may be used as the oxidizing agent in denitrification processes. The reducing agent in these reactions may be organic matter, or pyrite, which are oxidized to  $CO_2$  and sulfate. The ferrous ions ( $Fe^{2+}$ ), released during pyrite oxidation, may contribute further to the denitrification under oxidation to ferric ions ( $Fe^{3+}$ ), which may then precipitate as ferrihydrite compounds. The following three reaction schemes can be used to describe the denitrification processes.



### *Sulfate reduction*

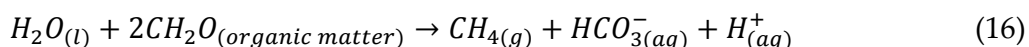
When nitrate is depleted sulfate may be used as the oxidizing agent. This occurs under its reduction to hydrogen sulfide gas.



In the presence of iron, hydrogen sulfide may precipitate as pyrite, but often some hydrogen sulfide will be left in the groundwater. Hydrogen sulfide has to be removed since it has a very pungent smell, which will ruin the quality of the water, and make it corrosive.

### *Methane formation*

Below the sulfate zone the environment will be highly reducing, and organic matter may be reduced to methane.



Even though this zone is usually found deep underground, the groundwater from shallower aquifers may still contain methane since it will diffuse upward after formation.



#### 4. Drinking water production - Simple water treatment

In Table 3, the usual composition of Danish groundwater is compared to the drinking water standards.

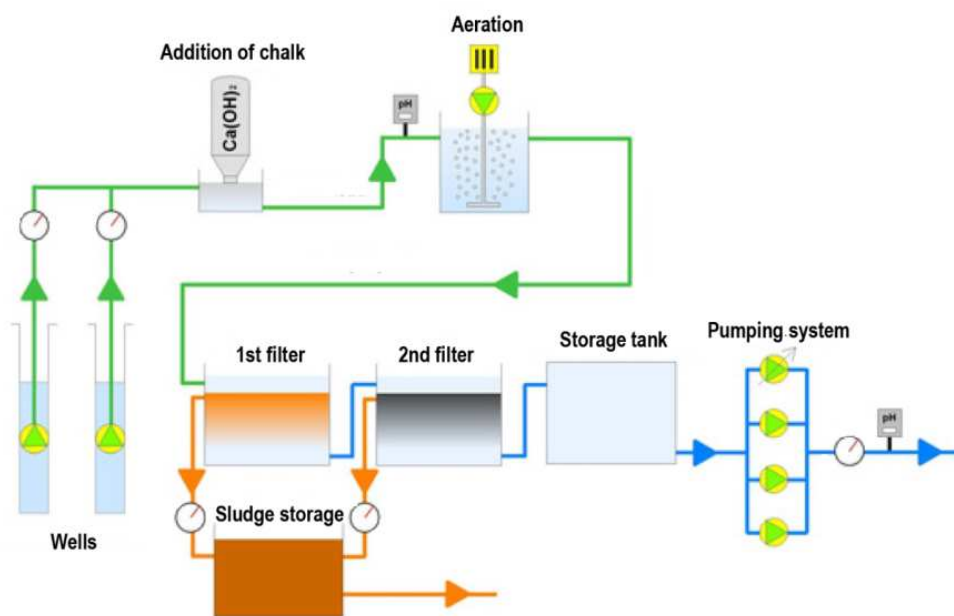
Parameter	Unit	Groundwater	Threshold limit after WW
Ca <sup>2+</sup>	mg/L	10-200	< 200
Mg <sup>2+</sup>	mg/L	2-30	50
Hardness	°dH		5-30
Na <sup>+</sup>	mg/L	10-100	175
NH <sub>4</sub> <sup>+</sup>	mg/L	0.08-6	0.05
Fe	mg/L	0.02-40	0.05
Mn	mg/L	0.001-3	0.02
HCO <sub>3</sub> <sup>-</sup>	mg/L	10-400	>100
Cl <sup>-</sup>	mg/L	30-70	250
NO <sub>3</sub> <sup>-</sup>	mg/L	0.5-110	50
NO <sub>2</sub> <sup>-</sup>	mg/L	-	0.01
SO <sub>4</sub> <sup>2-</sup>	mg/L	20-100	250
H <sub>2</sub> S	mg/L	-	0.05
Agg. CO <sub>2</sub>	mg/L	-	2
CH <sub>4</sub>	mg/L	-	0.01
O <sub>2</sub>	mg/L	0	10/5 *

\* The concentration of oxygen at the tap must be 5 mg/L, and the waterworks therefore strive to saturate the water with oxygen, which will often result in a concentration around 10 mg/L after the waterworks.

**Table 3.** Groundwater and drinking water composition as specified in Danish law by executive order no. 1024 (2,5).

As seen, iron, manganese and ammonium often exceed the limits regarding concentration of the ionic species. Also, nitrate is sometimes found in concentrations above the threshold limit, which is commonly due to anthropogenic pollution. For the non-ionic species, it is mainly hydrogen sulfide and methane that must be removed.

Because of the natural filtration taking place during the formation of groundwater, usually only a simple treatment consisting of aeration and sand filtration is necessary to produce drinking water. In standard Danish drinking water production, the water is pumped to the waterworks, where it is aerated to remove dissolved gasses, and then led through a sand filter where solids are retained, before it is finally stored in a holding tank. Earlier, the treated water was stored in water towers or elevated containers, but this practice has been abandoned due to hygienic considerations. Instead, buried storage tanks and pumping systems are used today to create the necessary pressure in the water system. In Figure 2, addition of  $\text{Ca}(\text{OH})_2$  is also shown. The purpose of  $\text{Ca}(\text{OH})_2$  is to remove aggressive  $\text{CO}_2$ , and may be necessary in areas with soft water. It is however not a part of the standard simple treatment, but belongs to the category of extended treatment techniques, which is covered after the simple treatment. As a final general remark, it should be noted that one of the unique features in the Danish drinking water treatment process is the missing disinfection step. No chlorine or other disinfectants are added to the water at any time during the drinking water process, resulting in high quality water.



**Figure 2.** General process diagram for a Danish waterworks. The addition of  $\text{Ca}(\text{OH})_2$  is not part of the standard simple treatment. Reprinted with permission from Esbjerg Water Supply (Forsyningen Esbjerg).

### Aeration

The aeration process serves two purposes:

1. A physical venting of the gasses  $\text{H}_2\text{S}$  and  $\text{CH}_4$  (and  $\text{CO}_2$ ) from the water
2. An increase of the oxygen content in the water to facilitate chemical/biological oxidation.

There exist several aerations methods. Earlier fountains or aeration stairs were widely used in the Danish drinking water sector due to their simplicity. In these methods, the water is

forced to run down a number of steps where the water will be mixed with air during the drops and the turbulence created by the impact on the following step (6).

Cascade systems and trickling filter trays have also been used for aeration. These are variations of the fountain/stair concept, and show a somewhat improved aeration level. In the tray method, the water is led out onto perforated stainless steel plates with  $\varnothing 3\text{--}5$  mm holes. This creates a large number of falling water jets that increases the total surface area, and hereby making the aeration more efficient. A drawback of the method is that the small holes tend to get clogged. The cascade system is similar to the fountain/stair system. Here the water runs down through a series of closed boxes with a small drop from box to box. This creates a negative pressure that sucks air down through the system and increases its efficiency compared to the open fountain/stair systems (6).

In cases where a large degree of venting is necessary, an INKA system can be applied. Here the water flows across a perforated plate, while air is blow up from below. This creates a large air to liquid ratio of up to 50-200, and ensures a very effective venting. Usually, this degree of venting is not necessary, and it might also affect the calcium carbonate balance negatively, since it will vent off a large degree of  $\text{CO}_2$ , leading to precipitation of calcium carbonate as pH increases. Also, the process is energy demanding and as such expensive (6).

Today, the most wide spread aeration method is bottom diffusers. The air inlet can be placed in a highly porous polyurethane sponge, which will ensure formation of small bubbles to give an efficient transfer of oxygen from air to water. The diffuser system has a better ability to saturate the water with oxygen, as well as to vent unwanted gasses compared to the previously used techniques. One of the main advantages of the diffuser system is that it can be modified to handle variations in the water flow and type of groundwater. An increase in the oxygen demand can be met by increasing the air flow; something, that cannot be done with the methods using the fall of the water for aeration. These must be designed to meet the specific oxygen demand for each waterworks. The oxygen demand is determined both by the flow and the groundwater's content of oxygen consuming species. The oxygen consuming species and their oxygen demand are shown in Table 4 along with the respective oxidation reactions:

- Oxidation of  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  to insoluble solids
- Oxidation of  $\text{NH}_4^+$  to  $\text{NO}_3^-$
- Oxidation of  $\text{H}_2\text{S}$  and  $\text{CH}_4$  to  $\text{SO}_4^{2-}$  and  $\text{CO}_2$

The relatively high oxygen demand of the methane and hydrogen sulfide oxidation reactions makes it important to vent these gases. Otherwise, the residual oxygen concentration might not meet the limit of 5 mg/L. Low oxygen concentration in the drinking water may result in anaerobic conditions in the piping system, leading to unwanted microbial growth. In case of microbial growth, nitrate may be reduced to nitrite, which may then increase to a level above the threshold limit. After aeration, the water may be lead to a reaction tank to allow for sufficient reaction time for the chemical oxidation reactions, but often the water is led straight to the sand filter(s).

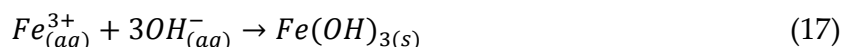
Substance	Oxidation	Oxygen demand per mg
Fe <sup>2+</sup>	$4H_{(aq)}^+ + O_{2(aq)} + 4Fe_{(aq)}^{2+} \rightarrow 4Fe_{(aq)}^{3+} + 2H_2O_{(l)}$	0.14
Mn <sup>2+</sup>	$4H_{(aq)}^+ + O_{2(aq)} + 2Mn_{(aq)}^{2+} \rightarrow 2Mn_{(aq)}^{4+} + 2H_2O_{(l)}$	0.29
NH <sub>4</sub> <sup>+</sup>	$2NH_{4(aq)}^+ + 3O_{2(aq)} \rightarrow 2NO_{2(aq)}^- + 2H_2O_{(l)} + 4H_{(aq)}^+$ $2NO_{2(aq)}^- + O_{2(aq)} \rightarrow 2NO_{3(aq)}^-$	3.6
CH <sub>4</sub>	$CH_{4(aq)} + 2O_{2(aq)} \rightarrow CO_{2(aq)} + 2H_2O_{(l)}$	4.0
H <sub>2</sub> S	$2H_2S_{(aq)} + O_{2(aq)} \rightarrow 2S_{(aq)} + 2H_2O_{(l)}$	0.51
	$2S_{(aq)} + 3O_{2(aq)} + 2H_2O_{(l)} \rightarrow H_2SO_{4(aq)}$	0.79

**Table 4.** Oxygen demand for main oxidizable components in groundwater (5).

### Sand filtration

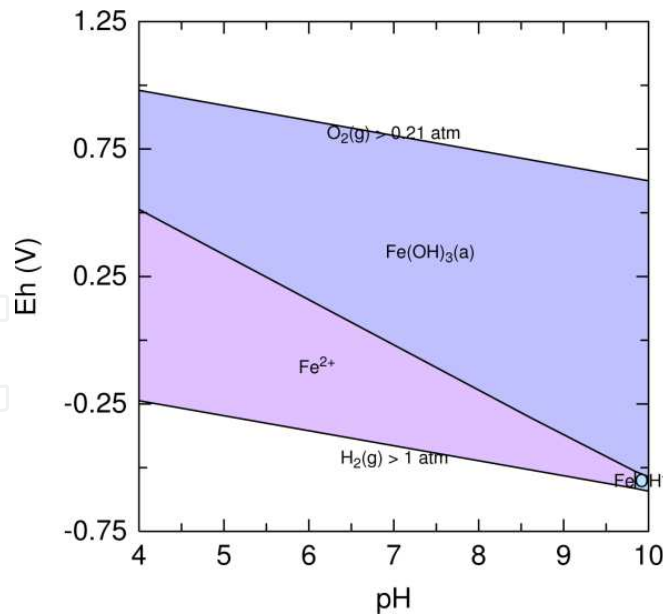
In the sand filtration, solid precipitates are filtrated from the water, and it is here that the largest part of the oxidation reactions takes place.

The oxidation of ferrous to ferric ions results in iron precipitating from the water as ferrihydrite because of its low solubility ( $pK_{sp} = 38.8$ ,  $T = 25\text{ }^\circ\text{C}$  zero ionic strength, (3)).

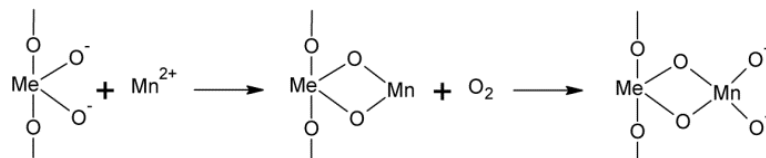


The ferrihydrite coats the sand grains, where it leads to autocatalysis of the oxidation reaction (7, 8). The autocatalytic reaction makes the iron oxidation very efficient, and removes the need for a reaction tank before the sand filter (6). Because of the redox potential for the oxidation of ferrous to ferric iron, the use of oxygen as the oxidizing agent is sufficient, see Figure 3. In some cases the chemical catalytic oxidation can be supported by iron oxidizing bacteria, which can increase the rate of oxidation/precipitation even further. An iron oxidizing bacteria often found in sand filters of Danish waterworks is *Gallionella ferruginea* that has been found to enhance the oxidation and precipitation velocity due to their production of exopolymers. The exopolymers give a denser structure of the iron precipitate, and allows for more iron to be removed by the sand filter before a backwash of the sand filter for its cleaning is necessary (9).

The redox potential for the oxidation of manganese(II) to manganese(IV) is higher compared to the iron(II) to iron (III) oxidation, see Figure 6, and with oxygen as the oxidizing agent, the process is relatively slow. At neutral pH, the reaction between Mn(II) and O<sub>2</sub> is around 10<sup>6</sup> times slower than the reaction between Fe(II) and O<sub>2</sub> (7). However, two processes in the sand filter aid the oxidation of manganese: Surface catalyzed oxidation and co-precipitation with ferrihydrite. Both processes can be illustrated by the two step reaction scheme in Figure 4.



**Figure 3.** Pourbaix diagram for iron, showing the most thermodynamical stable form as a function of pH and redox potential.



**Figure 4.** Reaction scheme for the oxidation of manganese in sand filters, where Me symbolizes a transition metal ion.

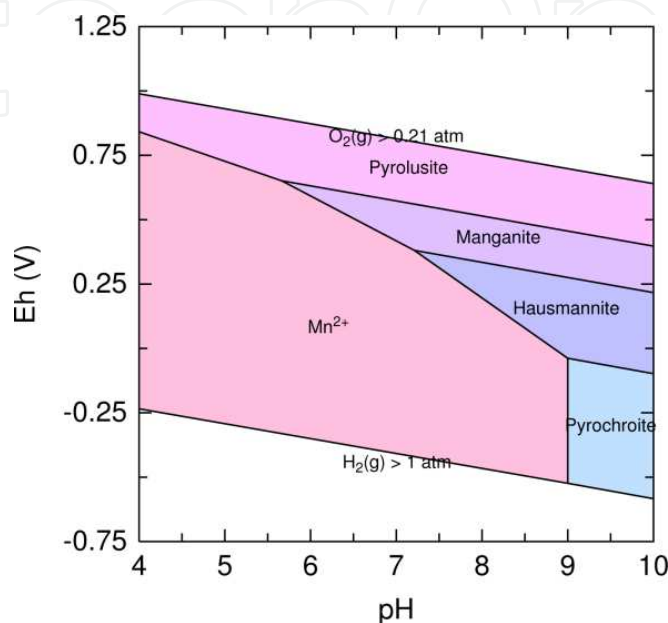
In the first step, Mn(II)-ions is oxidized to MnO<sub>2</sub>. As with iron, the oxidation of manganese is catalyzed by metal oxide surfaces on the sand grains. The hydroxyl groups on the metal oxide surface (Me-OH) attracts the Mn(II) ions and promote the oxidation, as illustrated in step two. If the metal surface is manganese oxides, the process is autocatalytic, but because of the ratio of iron and manganese in groundwater, the metal surface is most likely iron oxides in the first filtration step where manganese is then said to co-precipitate with iron (7). In the second filtration step precoating of the sand grains with manganese oxide can help oxidizing the adsorbed Mn(II) ions, see step three. The result is that it is not necessary to use stronger oxidizing agents than the oxygen found in atmospheric air to remove iron and manganese.

Also present in the sand filter are nitrification bacteria. These will oxidize ammonium first to nitrite and afterwards to nitrate (6).

To ensure an efficient oxidation, a double filtration system is commonly employed. The sand filters may be open or closed, with variations from waterworks to waterworks. The filters are back washed at regular time intervals, in a process where first air followed by water are sent backwards through the filter system. The air will remove and lift the colloids adsorbed to the sand grains producing a floating sludge on top of the filter. Later it will be washed away by help of the back wash water. At some drinking water treatment plants, the backwash water is returned to the plant where it is treated with UV-light, filtrated, oxidized

again, and brought to the drinking water container. When a sand filter is changed, some of the old sand is mixed with the new to preserve the microbiological environment and to increase the rate of re-population.

To demonstrate the effect of the processes included in a simple treatment at Danish waterworks, data has been collected at a specific waterworks at different points along the treatment process.



**Figure 5.** Pourbaix diagram for manganese, showing the most thermodynamical stable form as a function of pH and redox potential.

### Simple drinking water treatment – Case Spangsbjerg waterworks, Esbjerg

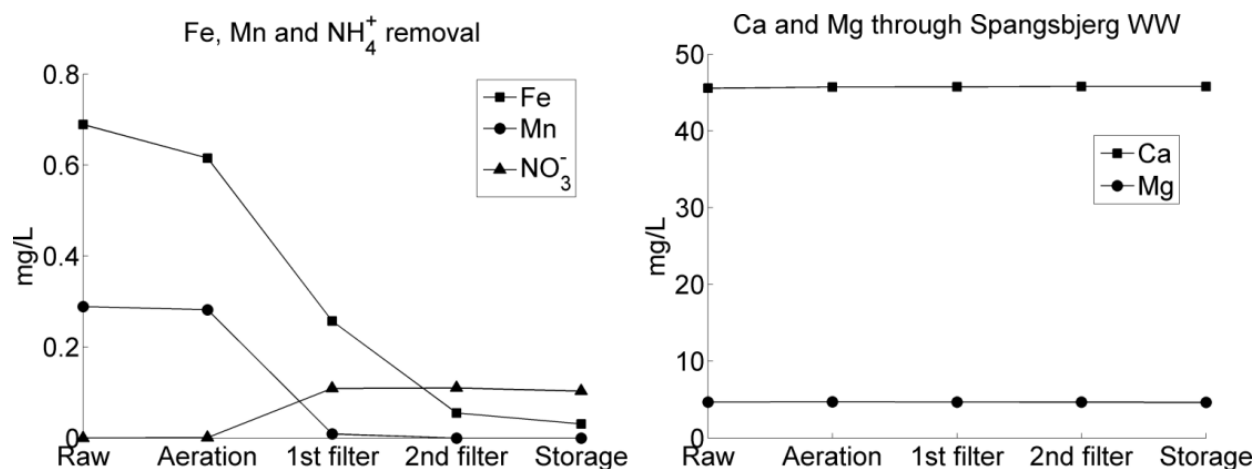
Spangsbjerg waterworks is one of four waterworks in the city of Esbjerg. It is one of the old waterworks placed in the city, but today 75 % of the groundwater is produced from wells 40 km away in central Jutland, from two deep aquifers: Boegeskov and Sekaer. The waterworks is equipped with a diffuser system for aeration and two open sand filters in series. After treatment the water is stored in a buried drinking water storage tank outside the waterworks.

To evaluate the effect of the treatment, the concentration of  $Fe^{2+}$ ,  $Mn^{2+}$ ,  $Ca^{2+}$ ,  $Mg^{2+}$  and  $NO_3^-$  was measured with ICP-AES at five places during the treatment.

1. Raw groundwater
2. After aeration
3. After 1<sup>st</sup> filter
4. After 2<sup>nd</sup> filter
5. Storage tank

The results are plotted in Figure 6 with the x-axis representing the transport through the waterworks.





**Figure 6.** Concentration levels of major constituents of groundwater through Spangsbjerg Waterworks simple drinking water treatment.

As seen, iron and manganese are effectively removed by the sand filters. Manganese are not affected significantly by the pure oxidation, but is almost completely removed already in the first filter. Some iron is removed by the homogenous oxidation, and needs to go through both filters to be reduced to below the accepted threshold limit. Ammonium is not directly measured, but the graph shows that the ammonium in the water is effectively converted to nitrate in the first filtration step. This is important since it shows that the conversion is complete in the first sand filter, meaning that no nitrite is left in the treated drinking water. Calcium and magnesium passed unaffected through the waterworks together with other macro ions as  $K^+$ ,  $Na^+$ ,  $Cl^-$ ,  $SO_4^{2-}$  and the main part of  $HCO_3^-$ . The unchanged hardness is also to be expected since Spangsbjerg Waterworks only applies aeration and sand filtration, which do not affect the solubility of calcium and magnesium minerals significantly.

## 5. Extended water treatment in the Danish drinking water sector

It requires a special permit if a Danish waterworks is to apply more advanced water treatment techniques than those already described in simple water treatment<sup>1</sup>. To achieve a permit, the waterworks must submit a technical, economic and environmental report for the choice of treatment technology according to § 14, part 2 of executive order no. 1451. Furthermore, according to § 9 of executive order no. 1451 it is necessary to obtain a statement from the National Board of Health, which is represented by the medical health inspectors (10). The need for a special permit is based on the principle that if techniques capable of removing pollution are allowed, the incentive towards avoiding pollution of the groundwater in the first place will be smaller. Therefore, if a well is found to be polluted, common practice is to close the well or use it for purposes other than drinking water, instead of applying more sophisticated water treatment techniques. With the structural reform of the Danish municipalities in 2007, the power to give permissions for extended

<sup>1</sup> From here on techniques other than what constitutes the simple water treatment will be classified as extended water treatment techniques.

water treatment was moved from the counties to the municipalities, which are expected to be more willingly to allow for further treatment (11). However, the conservative approach to the use of extended water treatment techniques is still widespread throughout the Danish drinking water sector, and the use is very limited.

Before the municipality reform was enforced, a compilation of the applications for use of extended water treatment techniques was made, and it was found that the sources for need of further treatment of the water was distributed into four categories (11). Treatment for:

1. Main constituents of groundwater: Aggressive carbon dioxide,  $\text{Ca}^{2+}$  and hardness,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , Fe/humus-complexes, humus and color.
2. Inorganic trace compounds: As and Ni.
3. Problems caused during simple treatment: Fe/Mn/ $\text{NH}_4^+$  removal and increased bacterial count.
4. Organic micropollutants: Pesticides and chlorinated organic solvents

An overview of the application is given in Table 5.

Problem causing compound	Number of applications	Geographical placement
<b>Main constituents</b>	<b>28</b>	
Agg. $\text{CO}_2$	9	Bornholm, west- and eastern Jutland
Ca and hardness	6	Funen, west- and southern Jutland, Zealand
$\text{SO}_4^{2-}$	1	Copenhagen
$\text{Cl}^-$	1	Southern Zealand
$\text{NO}_3^-$	4	Northern Jutland
Humic-bound Fe	5	Jutland
Humus	1	Western Jutland
Colour	1	Southern Jutland
<b>Inorganic trace compounds</b>	<b>11</b>	
As	10	Funen, Eastern Jutland, Southern Zealand
Ni	1	Copenhagen
<b>Operational problems</b>	<b>3</b>	
Mn/ $\text{NH}_4^+$	1	Western Jutland
CFU	2	Western Jutland
<b>Organic micropollutants</b>	<b>19</b>	
Pesticides	13	Funen, Copenhagen, north, east and central Jutland, Zealand
Chlorinated solvents	6	Funen Copenhagen
<b>Total</b>	<b>61</b>	

**Table 5.** Overview of compounds causing need for extended water treatment in the Danish drinking water sector (11).

As a result of these applications, there were 29 plants operating with extended water treatment in 2006. 14 of these were treating for issues with main constituents, nine for problems with inorganic trace compounds and five treating for pesticides and chlorinated solvents. The total amount of produced water from these plants was 2.5 million m<sup>3</sup> annually (11). The main problems may be divided into two groups: One correlated with the Danish geology, and a second with the anthropogenic activity.

Problems with calcium carbonate scaling and arsenic contamination belong to the first category, and are most prominent from Eastern Jutland and eastwards. This part of the country was covered by ice during the last ice age, while the western part of Jutland was left uncovered. As a result, carbon dioxide in the rain has dissolved much of the calcium carbonate in the underground in this part of the country. The soil is also more sandy in the western part of Denmark, while the soil in East Denmark has a high content of clay; a fact which also influences the vulnerability of the groundwater aquifers (1, 12).

The second category, pollution caused by anthropogenic activity, is distributed over the entire country, although it is also influenced by the geology, mainly the type of soil. The two main threats to groundwater quality are nitrate and pesticides. Chlorinated organic solvents are also a concern, but they are often found together with pesticide pollution (1).

In Table 6 an overview of the techniques applied as extended treatment in the Danish drinking water sector is given. It is seen that for some of the problems only one type of technique has been investigated, as with the use of active carbon filtration for removal of pesticides, whereas for other problems, a wider range of techniques have been applied. The use of different techniques is also correlated to the number of times the problem has been encountered.

Problem	Treatment technique
Aggressive CO <sub>2</sub>	NaOH, Ca(OH) <sub>2</sub>
Calcium and hardness	CO <sub>2</sub> , fluid-bed softener, magnetic treatment
Chloride	Reverse osmosis
Nitrate	Nitrate-redox method
Humic-Fe and humus	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> , KMnO <sub>4</sub> , AlCl <sub>3</sub>
Arsenic	FeSO <sub>4</sub> , FeCl <sub>2</sub>
Chlorinated solvents	Active carbon + UV, extended aeration (Microdrop)
Pesticides	Active carbon + UV

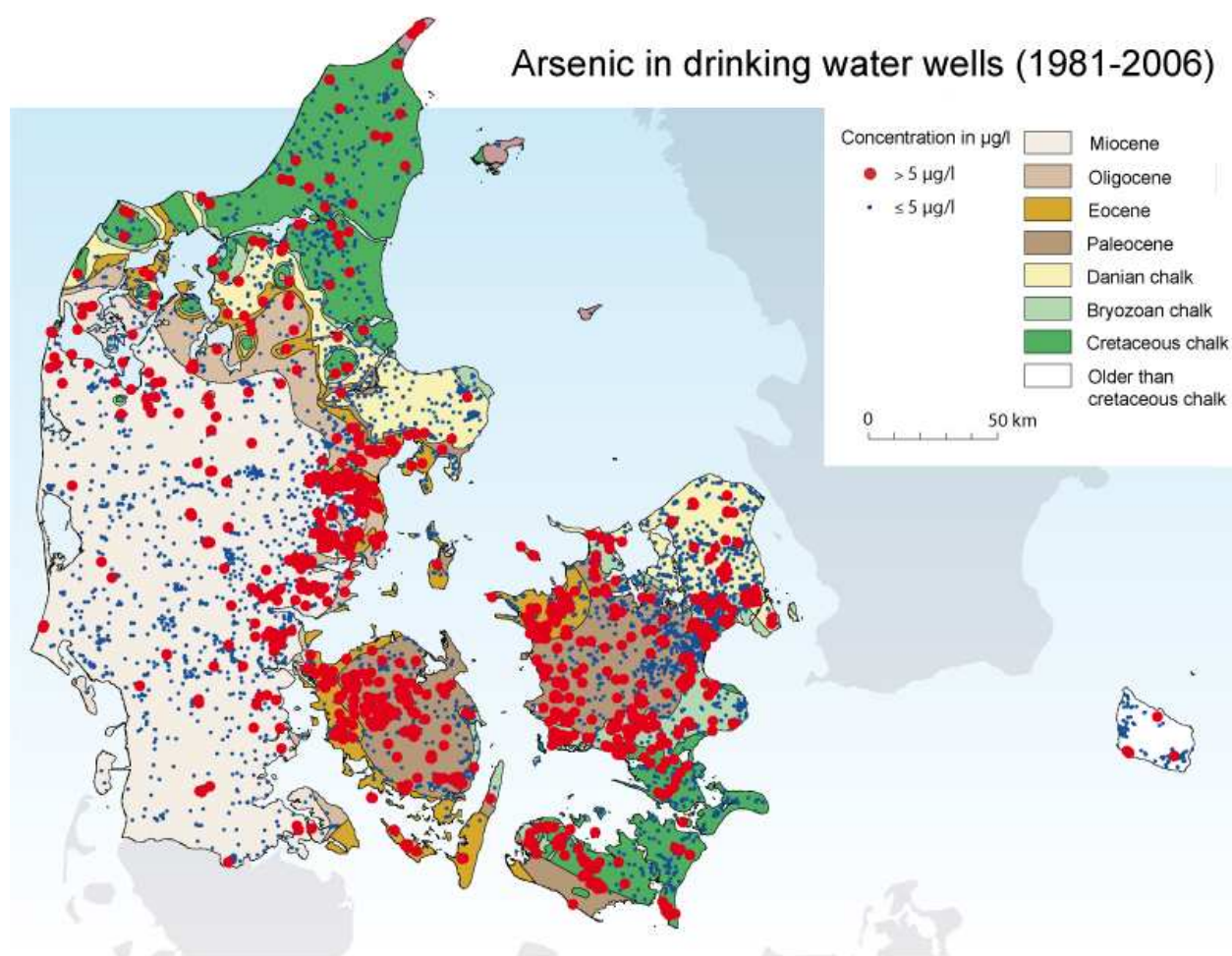
**Table 6.** Overview of extended water treatment techniques applied for the different problems encountered in the Danish drinking water production (11).

To investigate the use of some of these techniques in greater detail from here on, a case study approach will be used.

### 6. Galten waterworks – removal of arsenic

In 2003 the threshold limit for arsenic in drinking water was lowered from 50 to 5 µg/L. As a result, many waterworks situated in places with marine clay sediments got issues with

removal of arsenic (12). In Figure 7, it can be seen where in Denmark arsenic has been found in the drinking water, and it is clear that the clay rich eastern part of Denmark from east Jutland and eastward is the most affected. Arsenic is often bound to iron minerals and released when ferrihydrite ( $\text{Fe}(\text{OH})_3$ ) is reduced or pyrit ( $\text{FeS}$ ) is oxidized. However, it has been found that by applying reduced iron, arsenic can be made to co-precipitate (13). At Galten waterworks near Aarhus, the concentration of arsenic was found to be  $21 \mu\text{g/L}$ , and experiments with addition of  $\text{FeSO}_4$  were made at the smaller waterworks Galten Vestermarks. The method has been found to be effective. Based on these results, in 2004 Galten waterworks applied for permission to use  $\text{FeSO}_4$ , in concentrations of  $5 \text{ mg/L}$ , for removal of arsenic, to be able to meet the threshold limit. The permission was given, but only for a two year period based on the recommendation of the health inspector (11). In 2008 Galten waterworks got permission to use  $\text{FeCl}_2$  to remove arsenic (14).



**Figure 7.** Map of drinking water wells in which arsenic has been found in the period from 1981 to 2006. Modified from *Viden om Grundvand* (15).

Areas with arsenic concentrations above the threshold limit in more than 100 water wells are shown by red colour (15).

### **Frederiksberg waterworks – removal of chlorinated solvents**

In many places in Denmark, the groundwater is polluted with organic micropollutants such as chlorinated solvents. These originate from varying sources, including landfill leachate, colouring and varnish industry, pesticide production industry, gas stations and dry cleaning industry. Because the pollution is industrial related, it is often found close to population centers, where also many drinking water wells have been placed (1).

Frederiksberg waterworks is found close to central Copenhagen and produces 2,500,000 m<sup>3</sup> drinking water annually, which is 45 % of the total consumption for Frederiksberg. The remaining water is purchased by Copenhagen Energy. In 1997 the waterworks filed for permission to establish an active carbon filtration system because the wells had been found to be polluted with a wide range of mainly chlorinated solvents. In the wells 1,1,2-trichloro-ethene, cis/trans-1,2-dichloro-ethene, 1,1-dichloro-ethene, tetrachloro-ethene, vinylchloride, 1,2-dichloro-ethane, MTBE, toluene and benzene have been found in concentrations of 0.02-5 µg/L (15). In the application the waterworks assessed that it was not possible to find new wells without pollution. Also, although it was possible to purchase water from Copenhagen Energy, it was stressed that this would result in increased pressure on the environment of Zealand from where the water would be drawn. Already, Zealand is relatively poor in received rainfalls, and it was viewed as important to use the water resources as efficiently as possible (11).

In June 1997 permission was given to use active carbon for a five year period. Originally, Frederiksberg waterworks had applied for a permanent use of carbon filtration, but the health inspector would only agree to the five year permission. Later the permission has been extended on several occasions, latest in 2009, on the conditions that the filtration system is regularly checked for efficiency in removal of the chlorinated solvents.

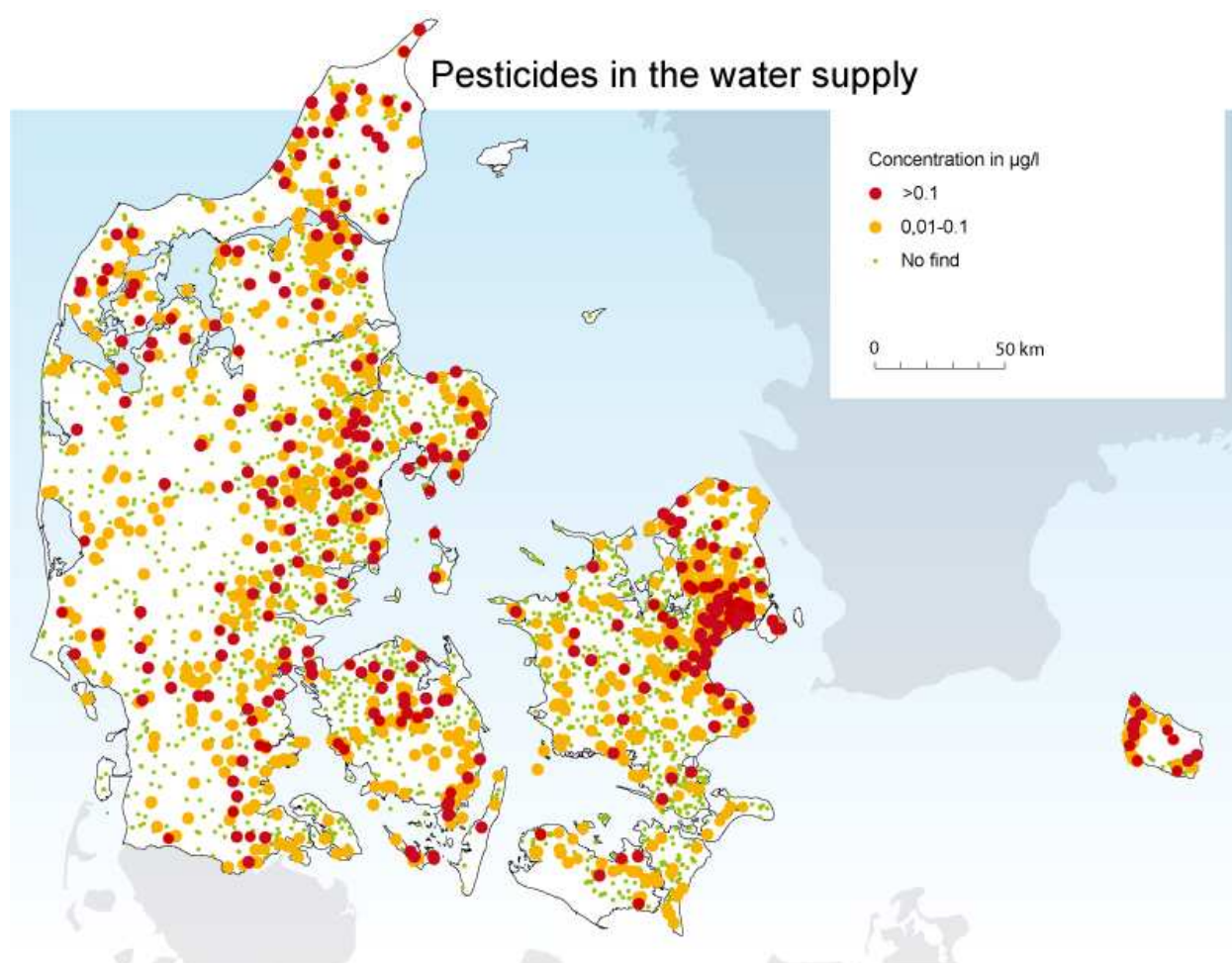
The long term goal for the waterworks is to supply water that has only gone through simple water treatment, and to lower the content of chlorinated solvents in the water. A new extraction strategy was constructed in 2003, in which two new wells were established. However, this has not been sufficient to reduce the concentrations, and carbon filtration continues to be necessary.

At Frederiksberg waterworks, the water first undergoes a simple treatment with aeration and sand filtration before it is stored in the water tanks. The carbon filtration system is placed after the storage tanks, and consists of two closed filters in parallel, followed by UV disinfection. Parallel filters have larger treatment capacity and are cheap with regards to installation costs, but also have higher risk for a breakthrough compared to serial setups, where the breakthrough can be measured on the first filter. To compensate for the higher risk of breakthrough, sampling points have been installed on the carbon columns to measure the saturation front. The filtration system has a capacity of 500 m<sup>3</sup>/h, contains 16 tons coal per filter and each filtration tank has a volume of 40 m<sup>3</sup>.



## 7. Hvidovre waterworks – removal of pesticides

One of the biggest issues in the Danish drinking water sector is contamination of the groundwater with pesticides, and it is estimated that between 1993 and 2009 around 130 wells all over the country have been closed due to pesticide pollution (16). Since 1993 the degree of pesticide pollution of the Danish groundwater has been monitored by the Danish geological service (GEUS), and during the years, an ever increasing amount of the aquifers has been found to be contaminated, as seen in Figure 9. This is not so much a result of an increasing actual pollution, as it is a result of more and more pesticides being included into the monitoring program. In the latest report, it was found that between 1990 and 2010, 50.7 % of the monitored aquifers had been polluted with pesticides, and that 24.5 % of the wells used by the water works contained pesticides (1). In Figure 8 it can be seen that all parts of Denmark, bot rural and cities, are affected by the pollution. However, the monitoring program does only cover parts of the aquifers in Denmark, and the pesticides currently in the monitoring program only constitute 29 % of the total sale of pesticides in Denmark from 1988 to 2010. The degree of pesticide pollution may as such be expected to increase over the coming years, forcing more waterworks to initiate extended treatment.



**Figure 8.** Map of groundwater wells (1993-2004) and drinking water wells (1993-2010) where pesticides have been found (1,15). Modified from *Viden om Grundvand* (15).



Of the pesticides currently in the program, 2,6-dichlororbenzamide (BAM), is the biggest problem, being found in 20 % of the analyses which have been found to contain pesticides (1). In all cases where extended treatment has been used to remove pesticides, it has been BAM that has been the polluting pesticide (11). BAM is a degradation product of the pesticide dichlobenil, which was earlier a widely used pesticide for removal of weed on uncultivated areas like farmers gravel covered courtyards, public parks and along railways.

Hvidovre Waterworks is situated in South East Copenhagen and produces around 800,000 m<sup>3</sup> of drinking water annually. Besides this, 2,400,000 m<sup>3</sup> is purchased annually from Copenhagen Energy to supply the waterworks own production. In October 1995, when BAM was taken into the analysis program of the waterworks, it was found in all the wells of Hvidovre waterworks, and in several of these wells BAM was found in concentrations above the threshold limit of 0.1 µg/L. In 1996, Hvidovre waterworks applied for permission to use active carbon filters followed by UV disinfection. In the application, the waterworks listed two scenarios: 1) Increase the amount of purchased water from Copenhagen Energy to lower the concentration below the threshold limit through dilution, or 2) Apply active carbon filtration to remove the pesticides. The use of active carbon was the cheapest solution, and also the ability to produce its own water was important to Hvidovre Municipality. On the 27<sup>th</sup> of June 1996, a temporary permission was given on the grounds that it was important to maintain a local drinking water production (health inspector), and because the county assessed the technology to be relatively simple. As a condition for the permission, an analysis program was setup to measure the concentration of BAM in the inlet and outlet of the waterworks and in the carbon filter, as well as bacteriological analyses to monitor the effect of the UV system. The first permission was given for three years and later extended on several occasions, since the system has been found to be effective at removing BAM and because it would be more expensive to purchase increased amounts of water from Copenhagen Energy (11).

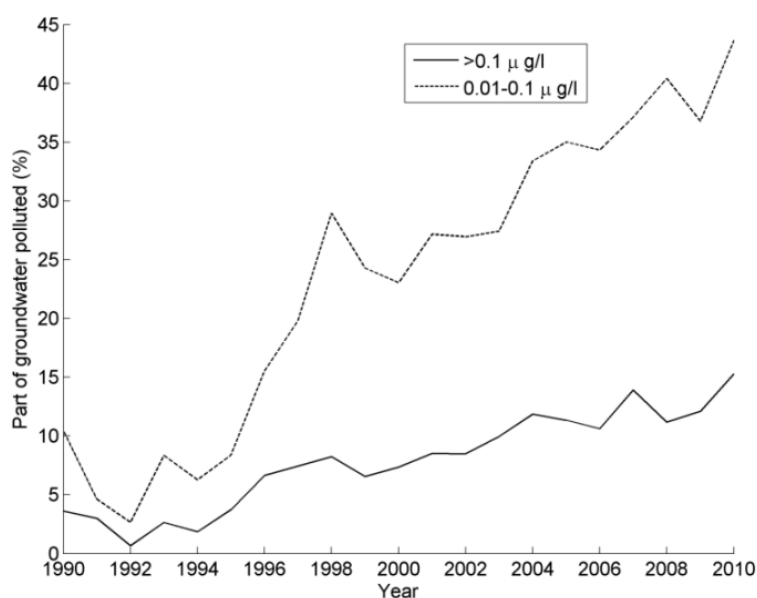
The water treatment at Hvidovre Waterworks consists of a simple treatment with aeration on cascade trays and two step serial sand filtration. The carbon filtration unit is installed at the outlet of the sand filter before the water is pumped to the drinking water tank, and is similar to the one installed at Frederiksberg waterworks. The full capacity of the system is 150 m<sup>3</sup>/h, but it operates at lower capacities around 90 m<sup>3</sup>/h. Each filter contains 6.3 tons coal and has a volume of 15 m<sup>3</sup>.

## **8. Sjaelsoe waterworks – removal of mycotoxins from surface water**

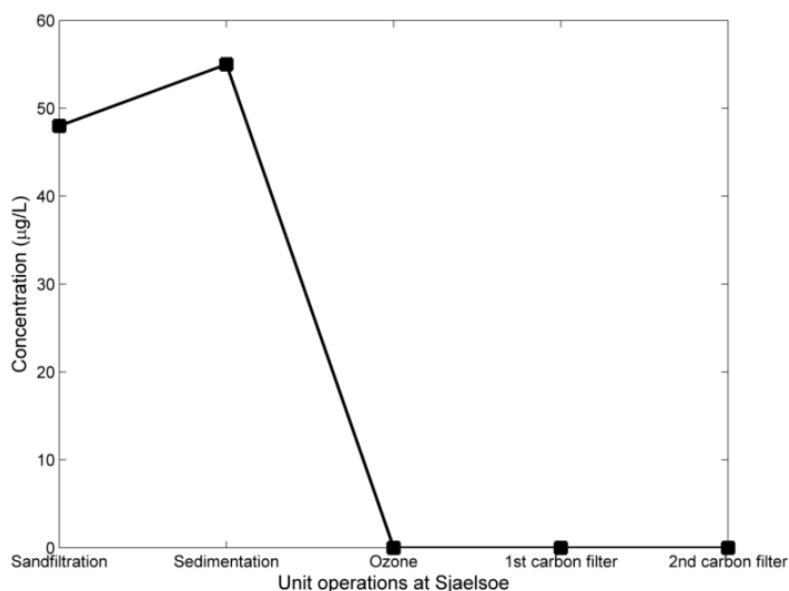
Today all drinking water in Denmark originates from groundwater. However, because of the low rainfall on Zealand, it has been necessary on occasions to use surface water. One such waterworks, capable of treating surface water is Sjaelsoe Waterworks in Rudersdal Municipality, north of Copenhagen, where it supplies drinking water to Gentofte, Lyngby-Taarbaek, Hoersholm and Karlebo municipalities. It produces around 5.5-6 million m<sup>3</sup> annually, but has a capacity of 11 million m<sup>3</sup> (17). Because the water sources have a high variation in the composition of the water, the waterworks consists of three main facilities handling each type of water:

- Plant I: Is a traditional waterworks with aeration on a cascade tray and subsequent sand filtration. It handles water from one water source.
- Plant II: Is equipped with a more efficient INKA aeration system, followed by sand filtration. The plant receives water from six water sources.
- Plant II: Is equipped to handle surface water from Sjaelsoe, a local lake. The plant consists of a sand filtration unit followed by flocculation, sedimentation, ozone treatment and a final scrubbing with biological active carbon filtration.

Due to the use of fertilizers, many of the inland waters in Denmark have suffered from eutrophication, which has also been the case in Sjaelsoe. Toxin analyses have shown the blue green alga from Sjaelsoe to contain microcystins in amounts from 1-59.1  $\mu\text{g}$  per gram dry matter. To evaluate the plant's efficiency in removing these compounds, experiments were made with microcystins extracted from dried algae on a pilot plant. The results showed that sand filtration and sedimentation did not affect the concentration of the microcystins, but that ozone was very effective for removing these compounds. By using an ozone concentration of 2 mg/L, the concentration of microcystins was reduced below the detection limit, see Figure 10 (18).



**Figure 9.** Development in the percentage of the Danish groundwater reserve where pesticides have been found from 1990 to 2010 (1).



**Figure 10.** Removal of microcystin in a pilot plant at Sjaelsoe Waterworks. Modified from *Blue green algae in bathing and drinking water* (18).

The plant at Sjaelsoe has as such been found to be effective in ensuring safe drinking water. Even so, due to the goal of using groundwater in the drinking water production, the plant has not been in operation since 1998.

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