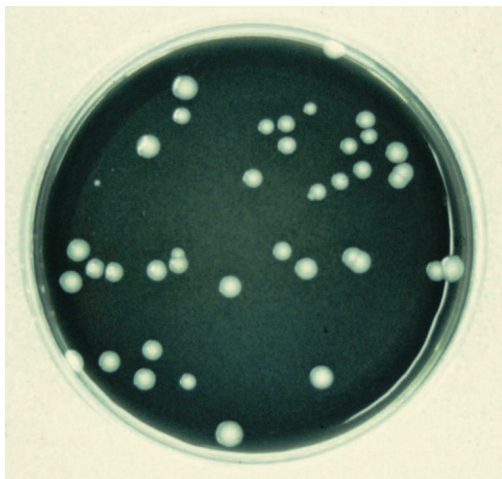
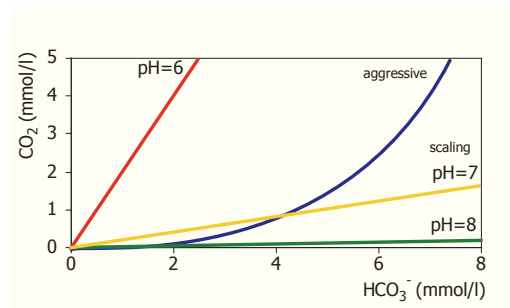
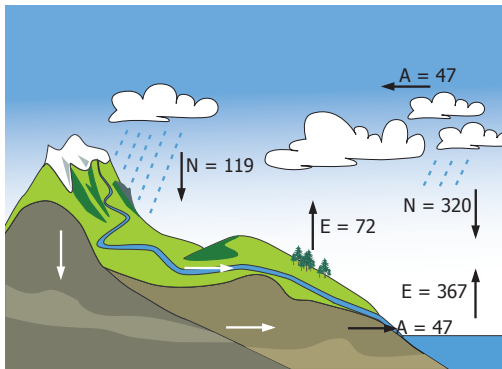


# Water quality



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## 1. Introduction

This module deals with the quality of water. First, the compounds that are transported during the hydrological cycle of water on Earth are discussed. Next, the physical and chemical properties of water are exposed in order to understand drinking water quality standards.

Then, the health aspects of drinking water are described, followed by the legislation regarding drinking water quality.

Finally, the quality requirements for some other applications of water are reviewed.

Water is the most important liquid on Earth; without water, life on Earth is impossible. The total surface area of the Earth amounts to 510 million sq. km, of which 73% consists of water (Figure 1). The total amount of water on Earth is 1,600 million km<sup>3</sup>, which is equivalent to a layer over the whole Earth having a thickness of 3.1 km (Table 1).

Only 0.5% of all water on Earth is in the form of fresh surface or groundwater. Of this fresh water, the majority is located in the deep underground (over 800 m deep).

In lakes and rivers there are 0.2 million km<sup>3</sup> of water, which is equivalent to 40,000 m<sup>3</sup> per human being.

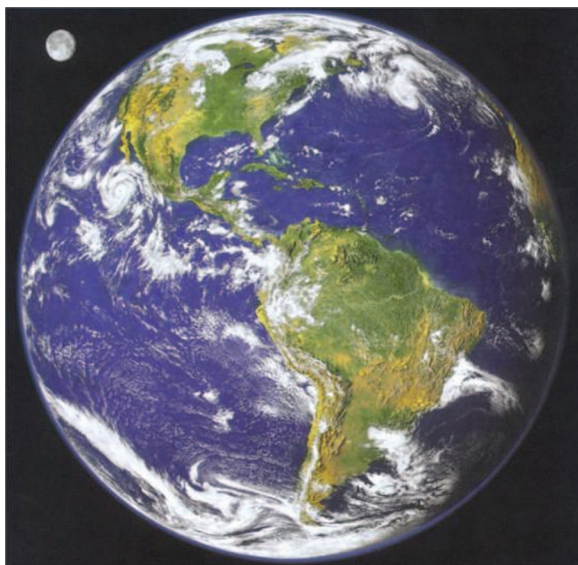


Figure 1 - Water on Earth

Table 1 - Water on Earth

Type of water	Quantity	
	(mln km <sup>3</sup> )	(m)
Total quantity of water	1,600	3,100
- chemically bound	230	450
- salt water	1,330	2,610
- ice and snow	30	59
- damp	0.015	0.030
Total quantity of fresh water	8.2	16.1
- in the underground	8.0	15.7
- in lakes and rivers	0.2	0.4

Water is continuously moving due to the hydrological cycle. The properties of water may change (e.g., contamination), or the water may change its phase (vapor, ice), but it remains water.

Due to evaporation, water is present in the atmosphere in the form of vapor. When clouds suddenly ascend, the vapor condenses and the water falls to the surface of the earth in the form of snow, rain or hail. Additionally, water may condense to fog, dew or frost.

Some condensed water will enter into lakes, brooks and rivers, and what doesn't evaporate, will flow over the soil and infiltrate into the ground. Rivers transport water to the sea; groundwater flows through the ground to lower locations and will also reach the sea. From the sea, water will vaporize again (Figure 2).

The water supply from the sea to the land (and the other way around) amounts to 47,000 km<sup>3</sup> per year, which is 1,490,000 m<sup>3</sup>/s or 600 times the discharge of the Rhine River. Water in the amount of 119,000 km<sup>3</sup> per year falls on the total land mass

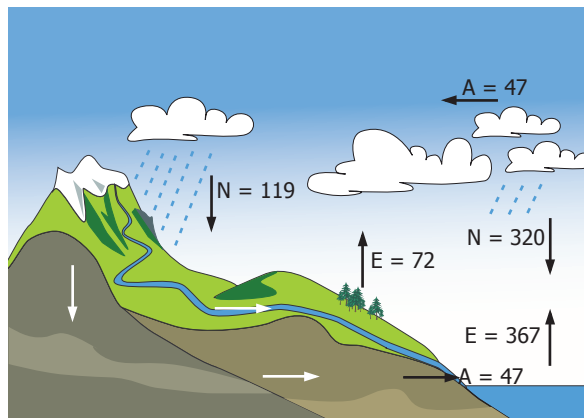


Figure 2 - Hydrologic cycle and balance (quantities in 1,000 billion m<sup>3</sup>/y)

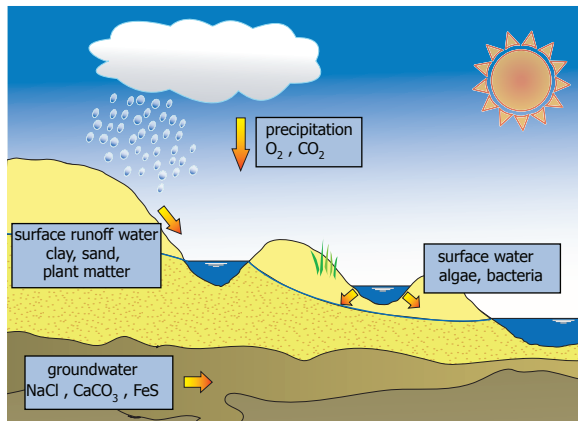


Figure 3 - The most important compounds in the hydrologic cycle

on Earth, corresponding to 0.7 m/y or 24,000 m<sup>3</sup>/inhabitant/y.

In precipitation, gases like oxygen and nitrogen are present. After the rain falls on the land, clay particles, sand and plant matter enter the runoff water. When the water infiltrates into the ground, minerals (e.g., Na, Cl, Ca, Fe) will enter it, because these compounds will dissolve from the soil matrix. Surface water contains several compounds, such as the biological compounds algae and micro-organisms. The most important compounds in the hydrologic cycle are shown in Figure 3.

Because of very large volume flows within the hydrologic cycle, even with small concentrations of some compounds, there will be a large mass flow. If all rivers contained an average of 100 mg/l of suspended particles and 1,000 mg/l of dissolved salts, then every second a mass of 1,640 tons of this matter would be discharged into the sea.

## 2. Water as a means of transport

### Contamination of water

Besides the compounds which are present in water naturally, water is also polluted with compounds as a result of human activities (Figure 4). Water is a means of transport for the discharge of diverse matter and also for the discharge of heat.

During the previous century, surface water was highly polluted at several locations in the



Figure 4 - In the seventies, water contained detergents resulting in foaming in wastewater treatment installations

Netherlands. The Rhine River was even called Europe's sewer. All kinds of industries, and also cities, used the major rivers as sewage systems. Wastewater entered the Rhine and Meuse rivers untreated, thus causing a steep decrease in animal and plant populations. Fortunately, enough people became more and more convinced that they should not continue as they had, and treaties were signed between the different Rhine shore states concerning discharges on the Rhine River.

The Surface Water Contamination Act was adopted in the Netherlands in 1970. The quality of surface water has improved since that time, but there still is a long road ahead before the natural equilibrium is restored.

Not only surface water was contaminated, but also groundwater quality was affected. For example, at some water companies' pumping stations pesticides and high concentrations of nitrate were found, due to overfertilization.

In terms of pollution, there is a difference between point and diffuse discharges. Point discharges have a high concentration of pollution issuing from one point. Examples of this are the effluent canals of wastewater treatment plants, overflows from sewers, and accidents.

Diffuse discharges are discharges which are located throughout the catchment area of a river. Examples of these are runoff from fertilizers (Figure 5) and the use of pesticides. Diffuse discharges are more difficult to treat than point discharges.



Figure 5 - An example of diffuse pollution

### Water warming

The surface water temperature is primarily determined by meteorological factors. In the Netherlands, this temperature varies between 0°C and 22°C.

The groundwater temperature is rather constant at 10°C, which is the average yearly air temperature (Figure 6). Only the deep groundwater (depth over 500 meters) has a higher temperature than the average surface temperature.

Due to industrial activities, the surface water temperature is artificially increased. This temperature increase is called thermal pollution and has both advantages and disadvantages.

Advantages are that the water freezes less quickly during winter and, natural self-purification increases because of higher biological activity.

In summer, however, the increased biological activity is disadvantageous because of the more rapid decay of organic matter. This consumes oxygen, while at the same time the oxygen concentration is already lower because of the higher water tem-

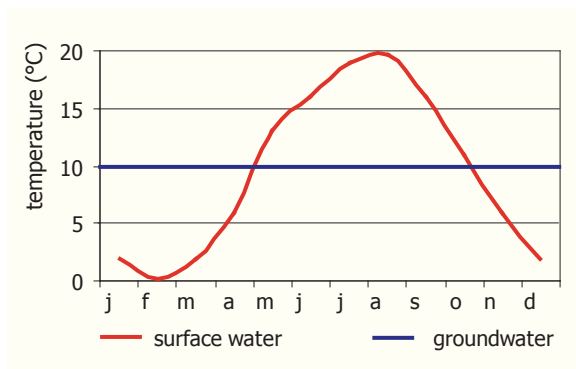


Figure 6 - Natural temperature variation in ground- and surface water

perature, which may cause anaerobic conditions, fish mortality, spoilage, and stench.

Another disadvantage is that the water has a lower cooling capacity during summer due to the high water temperature. Limitations have been set for the use of surface water for cooling purposes. The warming of river water can be prevented by using cooling lakes and towers.

### 3. Compounds in water

For discussing the different compounds in water, the following groups are discerned:

- undissolved matter
- Floating undissolved matter
- dissolved compounds
- vegetation
- higher organisms
- pathogenic microorganisms

The distinction between the groups above cannot be made very clearly in all cases. Examples of this are the taste and smell of water. Smell and taste are subjective parameters which cannot be detected by any device. The acceptable taste and smell of water are determined using consumer panels, which determine whether they find any unpleasant flavour or odour in a diluted sample of water.

By using different dilution rates, panel members select a taste or smell number. This number indicates the necessary dilution concentration to obtain water without any unacceptable smell or taste.

#### Undissolved matter

Undissolved matter consists of large or small particles which have not been dissolved in the water. A distinction based on size is made between suspended and colloidal matter (Figure 7).

The diameter and specific gravity of particles are important for removing them from the water. Particles having a diameter over 10 µm and a specific gravity other than that of water can be removed using either sedimentation or flotation.

Suspended particles have a relatively large size, but they may remain in suspension because of turbulent flow. Larger suspended particles will be

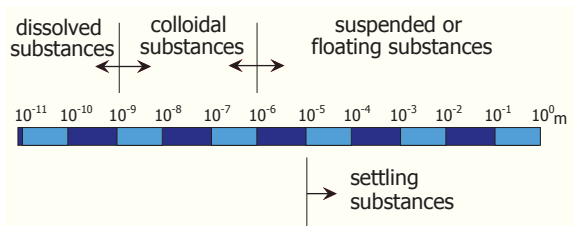


Figure 7 - Dimensions of compounds in water

transported by sliding over the bottom. Suspended particles having a density lower than that of water are transported by floating.

During transport, the suspended matter can be pulverized, transformed first into colloidal particles, and finally into dissolved compounds.

Suspended particles are of mineral or organic origin. Mineral suspended particles originate from sand, clay, loam and other inorganic soil types and enter the water as a result of erosion.

Organic suspended particles originate from the decay of vegetation and from the discharge of untreated domestic and industrial wastewater.

The rivers in Europe have a concentration of suspended matter of about 30 mg/l, while rivers in the tropics may contain up to 10,000 mg/l. The result of those high numbers is that the light entrance is limited and, consequently, oxygen production by means of photosynthesis decreases, the number of fish decreases, and mud will settle when the flow velocity of the water decreases.

In addition to the term suspended matter, the terms suspended solid matter and suspended solids are used.

The amount of suspended and colloidal matter can be expressed in multiple parameters, among which are turbidity - sight depth or light scattering (figure 8), suspended solids concentration, and number of particles per size (counting particles).

Colloidal particles are particles having a size between  $10^{-9}$  and  $10^{-6}$  m and a specific gravity around that of water. Colloidal particles generally have a negative electric charge.

Colloidal particles give colour and turbidity to the water.



Figure 8 - A low turbidity is desired for the customers' satisfaction with drinking water

### Floating undissolved matter

Floating compounds can be subdivided into solids and liquids. Both are often of an organic composition and can be eliminated microbiologically.

Floating matter causes pollution of the shores and an unattractive appearance for recreational activities.

Aquatic plants, decayed organic and animal life, faecal matter and materials from bio-industry belong to this group of solids. Aquatic plants give a pleasant appearance to the water as long as their numbers do not overwhelm.

When there is a high concentration of phosphates in the water (eutrophic water), an explosive growth of aquatic plants may occur, causing an obstacle to navigation. Also, the water may become anaerobic because of the obstruction of light, which will in turn cause fish mortality, spoilage and stench.

Oil and waste from chemical plants belong to the liquids group.

Oil enters the water due to accidents and carelessness. Leaking tanks and transportation pipes, ship collisions, illegal discharges of oil into the sewer system by individuals, and the cleaning of oil tanks on board ships cause the presence of mineral oil in water.

The specific gravity of mineral oil is lower than that of water, forming a layer upon the water's surface. This layer prevents oxygen and light from entering the water, thus causing anaerobic conditions, fish mortality and stench. Oil gives an unpleasant taste to water, and removing it from the water is difficult.

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## Dissolved compounds

Dissolved compounds have a diameter below  $10^{-9}$  m.

In dissolved compounds, a distinction is made on the basis of the chemical composition of the compounds. For example, a distinction is made between inorganic and organic compounds.

A subdivision is also made based on the amounts of chemicals present: macro-pollutants for concentrations over 1 mg/l and micropollutants for concentrations below 1 mg/l (so in the order of micrograms per liter).

Examples of inorganic macro-pollutants are dissolved gases (like  $O_2$  and  $CO_2$ ), dissolved salts (like NaCl,  $CaCO_3$ ,  $MgCO_3$ ) or reaction products from inorganic transformations (Fe, Mn) or organic transformations ( $NH_3$ ,  $CH_4$ ,  $H_2S$ ).

In water several dissolved gases may be present. Rainwater, for example, contains oxygen and nitrogen in concentrations of some mg/l.

Groundwater contains carbon dioxide ( $CO_2$ ), but may contain gases like methane ( $CH_4$ ) and hydrogen sulphide ( $H_2S$ ) as well. When groundwater is abstracted from great depths and when there is a high concentration of organic matter in the ground, the water no longer contains any oxygen (anaerobic water).

Due to the long retention times of water underground, the water is able to dissolve several salts or minerals in the soil. Also, chemical or biological reactions may dissolve some compounds into the water. The consequence of this is that the concentration of inorganic salts in groundwater increases (compared to the concentration in rain). The concentration of salts can be as large as some tenths of a milligram up to hundreds of milligrams per liter.

Shellfish in nature produce large amounts of calcium carbonate. Natural phenomena like stalactite caves (Figure 9) and limestone sediments are also examples of calcium carbonate, as well as what gives hard water its hardness.



Figure 9 - The stalactites in Remouchamps are an example of precipitation of calcium carbonate

By discharging wastewater, also considerable amounts of salts can enter the water. Infamous are the waste salt discharges of the French potassium mines into the Rhine River, which doubled the river's chlorine concentration in the past decades.

The total concentration of dissolved salts can be determined by vaporizing the water and weighing the residual (dry residual). This concentration can also be calculated as the arithmetic sum of all dissolved salts. This parameter can also be referred to as Total Dissolved Solids (TDS), which is mostly determined using evaporation.

Water having a TDS below 1,000 mg/l is called fresh water, a TDS over 10,000 mg/l is called salt water. The transition area between 1,000 and 10,000 mg/l is called brackish water.

Instead of determining the dry residual or the TDS, a determination of the electrical conductivity (EC) of the water is often sufficient.

Besides inorganic macro-pollutants, also inorganic micropollutants, such as heavy metals and radio-

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active compounds, can be discerned. Even in low concentrations, these compounds can be harmful to public health.

Organic compounds are all carbon compounds, except carbon dioxide ( $\text{CO}_2$ ), hydrogen carbonate ( $\text{HCO}_3^-$ ) and carbonate ( $\text{CO}_3^{2-}$ ), which are not inorganic carbon compounds. Organic compounds mainly consist of hydrogen and oxygen, in addition to carbon, and to a lesser degree of nitrogen, sulphur and phosphorous. The concentration of organic compounds in ground or surface water amounts to 1 to 10 mg/l.

The majority of organic compounds are of a natural origin (natural organic matter, NOM, decayed animal or vegetable material), but they also partly originate from the discharge of residential and industrial wastewater.

The number of organic compounds in water is very large. Therefore, it is impossible to measure all those compounds. For this reason, the concentration of organic compounds is determined on the basis of some properties of groups of compounds.

Most pesticides belong to the class of organic micropollutants. There are strict standards for these pollutants, as they are harmful to public health even in low concentrations.

### **Vegetation in water**

Different kinds of vegetation or vegetative residuals may be present in water. The size of the vegetation varies from very large (e.g., surface water which has been completely covered by water hyacinths) to microscopically small (phytoplankton). This vegetation forms an essential element in the hydrobiologic cycle, as it decays all kinds of inorganic or organic compounds.

They are not harmful to human health, except for very few poisonous species. However, they may impact the appearance of the water (flavour, odour, colour). This larger and smaller vegetation is the food source for other organisms like fish, shellfish and crustaceans.

For the drinking water supply, algae are the most important representatives of vegetation in water.

Algae are able to build up organic matter from minerals, water, carbon dioxide, nitrate, phosphate, etc. using sunlight energy. This process is known as photosynthesis or assimilation.

When algae die, the reaction is reversed and is called dissimilation. Algae need the nutrients sulphur, nitrogen and phosphorous for their growth, in addition to carbon and water.

The nitrogen and phosphorous concentrations of water are low by nature, thus limiting algae growth. From the discharge of treated wastewater into surface waters, the concentrations of phosphorous and nitrogen rise, causing increased algae growth. The water becomes turbid and opaque and has an unpleasant green, brown or red color. Then, the water is no longer suitable for recreation and the preparation of drinking water from it is expensive, due to the required advanced treatment techniques.

The concentration of algae in water is determined by counting them under a microscope or by measuring the chlorophyll(a) concentration. Well-known types of algae are blue algae and seaweeds (diatoms). Most algae have a size between 0.01 and 1 mm.

### **Higher organisms**

Besides vegetable compounds, also microscopic animal organisms may be present in water (zooplankton). In nature, these organisms are present in large numbers, and they may also be found in drinking water.

Table 2 provides an overview of a few of those organisms and the amount in which they may be found in drinking water. The organisms in water are determined by pouring water through a filtration cloth of 0.1 mm. The material (sediment) that remains on the filtration cloth is investigated under a microscope. Based on their external characteristics, the different kinds of organisms are counted. Most of these higher organisms have a size between 0.05 and 10 mm.

These higher organisms are harmless to human health and their presence in drinking water is only



## Concentration – terms and definitions

It is important to know which amount of a certain compound is present in some mixture. Different measurements are used to do so:

- mass (kilogram or equivalents: g, mg,  $\mu\text{g}$ , etc.)
- volume (cubic meter or factors of this:  $\text{dm}^3$ , l, ml, etc.)
- amount of substance (mol or factors of this: mmol,  $\mu\text{mol}$ , etc.)

These three different measures have mutual relationships, which are defined by the following properties:

- density of a compound ( $\text{kg}/\text{m}^3$ ) = mass / volume
- molar mass of a compound ( $\text{kg}/\text{mol}$ ) = mass / amount of substance

The density (formerly specific gravity) is dependent on both temperature and pressure.

The molar mass of a compound has a linear relationship with the molecule as mass, as the number of molecules per mol is equal for all compounds. The molecular mass is the sum of the atomic mass of the different atoms in a molecule.

$$M = N_A \times \sum m_a = \sum M_a$$

in which:

$m_a$  = atomic mass of an atom (g)

$N_a$  = Avogadro's constant (number of molecules per mol =  $6,022 \cdot 10^{23}$ )

$M_a$  = molar atomic mass (g)

The molar atomic mass can be found in reference books.

Sometimes, one does not start from the compound itself, but from the solvent before dissolving (and possible subsequent reactions and/or dissociation).

The named measurements and definitions are all used, possibly in the same text.

For a component in a compound, the following terms are used:

- (mass) concentration ( $\text{kg} / \text{m}^3$ ) = mass / total volume
- mass fraction (%) = mass / total mass / 100
- (ppm) = mass / total mass - 1,000,000
- molar concentration ( $\text{mol} / \text{m}^3$ ) = amount / total volume
- molality ( $\text{mol} / \text{kg}$ ) = amount / mass of solvent

In water chemistry, computations of the equilibrium reactions are based on the molar concentrations, expressed in mol/l. This measure is called molarity, having the Molar (1M is 1 mol/l) as its unit. Pure water itself is 55.6 M (1,000 g/l and 18 g/mol).

Ions are electrically charged. The electric charge of some compound within a fluid depends on the concentration and on the valence of the relevant ion:

- valence concentration ( $\text{eq} / \text{m}^3$ ) = molar concentration · valence

The sum of the valence concentrations of all positively charged ions is equal to that of the negatively charged ions (electric neutral).

aggravating if they are visually discernible by the naked eye.

### Pathogenic microorganisms

Humans can be infected by pathogenic (= disease causing) microorganisms through the intake of drinking water or by contact with infected water (swimming).

Pathogenic microorganisms are not present in water by nature, but they enter the water via feces and urine from humans and animals, mainly because of the continuous supply of untreated or not fully treated wastewater from houses or bio-industry (abattoirs and fattening cattle stables). These microorganisms die in the water because the water temperature is lower than the body temperature of humans or animals.

Pathogenic microorganisms can cause different diseases (Table 3), which may become epidemic rather quickly via the water.

Cholera epidemics were extensive in the 19th century.

For several decades, typhus was present in the Netherlands because of the lack of safe drinking water (Figure 10) and since 1976, some cases of Legionnaire's disease have been registered.

The presence of many different kinds of pathogenic micro-organisms in low concentrations in the water, makes impossible to measure all of them separately. Therefore, only some indicator organisms are measured, like for example, E. Coli. These are organisms that originate from faeces, are present in large numbers and are typical for a larger group of pathogenic micro-organisms.

Pathogenic microorganisms in water are determined by passing the water through a membrane filter and placing the filter residual on a growth medium for a special organism/group of organisms,

### Computation ionic balance

A single unknown concentration can be computed using an ionic balance.

In order to do this, the valence concentration for each component is computed:

Compound	Weight concentration (mg/l)	Molar mass (g/mol)	Molar concentration (mmol/l)	Valence	Valence concentration (meq/l)
Cations:					
Na <sup>+</sup>	63	23	2.74	1	2.74
K <sup>+</sup>	5	39	0.13	1	0.13
Ca <sup>2+</sup>	45	40	1.13	2	2.25
Mg <sup>2+</sup>	9	24.5	0.37	2	0.73
Fe <sup>2+</sup>	4	56	0.07	2	0.14
Mn <sup>2+</sup>	1	55	0.02	2	0.04
NH <sub>4</sub> <sup>+</sup>	2	18	0.11	1	0.11
Total	129				6.14
Anions:					
Cl <sup>-</sup>	73	35.4	2.06	1	2.06
HCO <sub>3</sub> <sup>-</sup>	151	61	2.48	1	2.48
NO <sub>3</sub> <sup>-</sup>	1	78	0.01	1	0.01
SO <sub>4</sub> <sup>2-</sup>	Unknown	96	?	2	?
Total	?				6.14

From the ionic balance it follows that the total valence concentration of the anions should also be 6.14 meq/l.

Therefore, the amount of SO<sub>4</sub><sup>2-</sup> should be 1.60 meq/l (= 6.14 - 2.06 - 2.48 - 0.01).

Conclusion: SO<sub>4</sub><sup>2-</sup> = 1.60 meq/l = 1.60/2 = 0.80 mmol/l = 0.88 x 96 = 77 mg/l.

The total amount of dissolved matter amounts to 431 mg/l (= 129 + 73 + 151 + 1 + 77).

### Computation of gas concentration in water

Compute the oxygen concentration in water, which is in free exchange to open air (at 10°C, 1 bar = 101,325 Pa).

At sea level, air contains approximately 21 volume percent of oxygen.

The molar fraction of oxygen amounts to 0.21.

The partial pressure is 0.21 bar or  $(101,325 \cdot 0.21 =) 21,300$  Pa.

The oxygen concentration in air is:  $(21,300 / (8.3143 \cdot (273+10) ) =) 9.05$  mol/m<sup>3</sup>.

Having a Henry coefficient of 0.041 for oxygen, the oxygen concentration in water will be:

$(0.041 \cdot 9.05 =) 0.37$  mol/m<sup>3</sup>.

At a molar mass of 32 g this amounts to  $(0.37 \cdot 32 =) 12$  g/m<sup>3</sup> (mg/l).

and then in an incubator at an optimum growth temperature.

To determine the colony number, not even this concentration technique is required, and pouring out a bit of water over a fertile soil is sufficient.

After sufficient growing time in the incubator the number of colonies that have been formed is counted and reported as colony forming units

(CFU) per volume. Plaque forming units (PFU) are referred to bacteriophages.

### The purity of water

Water is a very pure product. When the standards for drinking water are considered, observed and the maximum concentration of all the macro-parameters are included, it can be seen that drinking water contains over 99.9% water molecules. When the composition of rainwater is observed, it even consists of 99.995% water molecules (Table 4). Fresh surface water consists of over 99.5% water molecules.

As a comparison, the purity of beer is given. In beer the concentrations of the inorganic macro-parameters are slightly higher than in drinking water, but the major difference is the far greater concentration of organic compounds (alcohol). Besides alcohol, the concentration of carbon dioxide in beer is significantly higher than in drinking water. The carbon dioxide gives the bubbles and fresh taste to beer. Because of these additional compounds, the purity of beer is much less than that of drinking water: it consists of only 88% water molecules.

Table 2 - Limiting values for higher organisms in drinking water (VEWIN 1993)

Organism	Number (per m <sup>3</sup> )
Ciliata	500
Amoeba	100
Testacea	5,000
Foraminifera	100
Turbellaria	100
Nematoda	5,000
Rotatoria	25,000
Gastrotrichia	500
Tardigrada	250
Oligochaeta	100
Gastropoda	50
Hydrachnellae	50
Hydrach larvae	250
Cladocera	2,500
Ostracoda	100
Copepoda	-
Cyclopoida and Calanoida	1,000
Harpacticoida	2,500
Nauplii and Copepodieten	5,000
Asellidea	50
Asellidea (parts)	500
Chironomidae	50
Sediment (ml/m <sup>3</sup> )	250

Table 3 - Pathogenic microorganisms and their resulting diseases

Pathogenic microorganisms	Illness
Bacteria	Typhoid fever, Cholera
Viruses	Hepatitis, Polio
Protozoa (single cell animals)	Diarrhea and stomach complaints

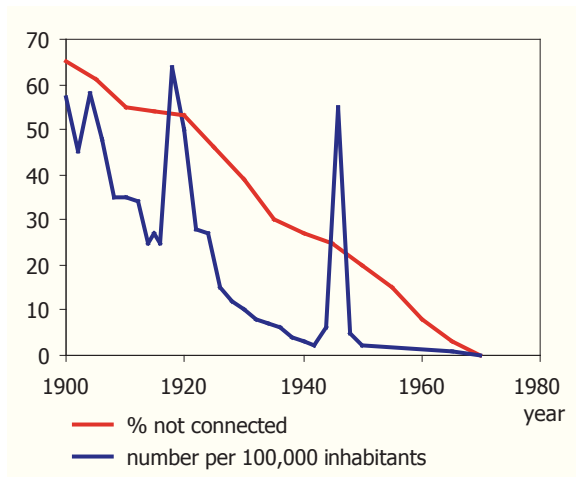


Figure 10 - Deaths due to typhoid fever and percentage of population not connected to drinking water supply

## 4. Physical and chemical properties of the water

### 4.1 General properties

Pure water is a clear, colour-, odour- and flavourless liquid. When exposed to sunlight, thick layers of water appear sky-blue. Water is a liquid between 0°C and 100°C, but above that temperature it is

Table 4 - The purity of different products (in mg/l)

	Drinking water guidelines	Rain-water	Ground-water at Veluwe	Beer
Salts:				
- Cl <sup>-</sup>	(150)	3	13	190
- NO <sub>3</sub> <sup>-</sup>	50	3	7	< 1
- SO <sub>4</sub> <sup>2-</sup>	150	6	9	152
- HCO <sub>3</sub> <sup>-</sup>	> 60	0	78	630
- Ca <sup>2+</sup>	(100)	0.2	27	44
- Mg <sup>2+</sup>	(50)	0.1	2.5	190
- Na <sup>+</sup>	150	0.9	9	85
- K <sup>+</sup>	(12)	0.2	0.7	300
Gases:				
- CO <sub>2</sub>	(< 20)	0.8	7	6,000
- N <sub>2</sub>	-	19	19	-
- O <sub>2</sub>	> 2	11	4.4	< 20
Heavy metals:				
- Mn <sup>2+</sup>	0.05	0.03	0.03	0.10
- Fe <sup>2+</sup>	0.20	0.04	0.04	0.05
Organic compounds				
	very low	none	none	112,000
Total (mg/l)	900	47	190	120,000
Water (%)	> 99.9	99.995	99.98	88

a gas (water vapour), and below it a solid (ice) (Figure 11).

Most of the physical and chemical properties of water are caused by its chemical composition (H<sub>2</sub>O) and the atomic configuration of the water

### Dissociation of carbon dioxide

A spring water factory puts 4.4 g CO<sub>2</sub> in 1 liter of demineralized water.

What will be the pH value of this water?

What amount of true CO<sub>2</sub> will be in the water?

What will be the pH value when 1 mmol/l HCO<sub>3</sub><sup>-</sup> is added?

The inserted amount of CO<sub>2</sub> (or H<sub>2</sub>CO<sub>3</sub>) is  $4.4 / 44 = 0.1$  mol.

When  $x$  mol of CO<sub>2</sub> dissociates,  $x$  mol H<sup>+</sup>,  $x$  mol HCO<sub>3</sub><sup>-</sup> and  $1 - x$  mol CO<sub>2</sub> will be formed (neglecting the amount of HCO<sub>3</sub><sup>-</sup> that is transformed into CO<sub>3</sub><sup>2-</sup>).

From  $K_1 = x \cdot x / (0.1 - x) = 4.5 \cdot 10^{-7}$  it follows that  $x = 0.00021$  mol/l or 0.21 mmol/l.

Thus, the pH value will be  $\text{pH} = -\log(0.00021) = 3.68$ .

From  $K_2 = 4.7 \cdot 10^{-11} = [\text{H}^+][\text{CO}_3^{2-}] / [\text{HCO}_3^-]$  and after entering the known values for H<sup>+</sup> and HCO<sub>3</sub><sup>-</sup> it follows that  $[\text{CO}_3^{2-}] = 4.7 \cdot 10^{-11}$ . This can indeed be neglected, so that:

$[\text{CO}_2] = 100 - 0.21 = 99.79$  mmol/l and  $[\text{HCO}_3^-] = 0.21$  mmol/l

(meaning that 0.2% has dissociated)

After adding 1 mmol/l HCO<sub>3</sub><sup>-</sup> the pH value will be:

$\text{pH} = 6.35 - \log \{99.79 / (0.21+1.00)\} = 6.35 - 1.92 = 4.43$

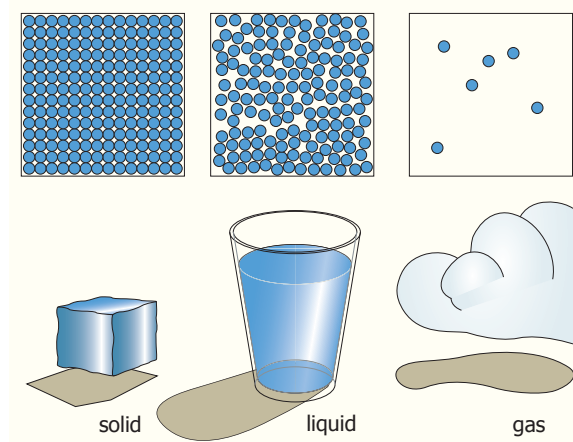


Figure 11 - The three phases of water

molecule. The two hydrogen atoms are located on both sides of the oxygen atom, however, not in a straight line but at an angle of  $104^\circ$ .

Due to the large difference in atomic size between hydrogen and oxygen, water is a strong dipole (Figure 12). This makes water a good solvent and causes increased boiling and freezing temperatures as compared to other compounds having a similar molecular weight, like methane ( $\text{CH}_4$ ).

Many of the physical properties of water strongly depend on temperature (density, viscosity, surface tension, specific heat, vapour pressure, volumetric expansion, compressibility). The large variation in viscosity (gumminess) (Table 5) is important in drinking water treatment as well as for distribution because of the flow resistance in filter media and pipes.

The presence of other compounds will change some properties of water significantly and others not at all. Sea water, for example, has a concentration of dissolved matter of 3.5% (mostly NaCl). This makes the density of water 2.5% higher, the viscosity 10% higher, but the electric conductivity

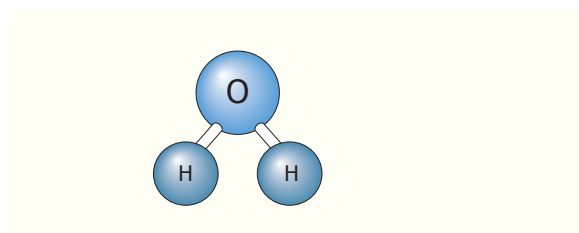


Figure 12 - Water as a dipole

Table 5 - Density and kinematic viscosity as a function of temperature

Temperature (°C)	Density (kg/m <sup>3</sup> )	Kinematic viscosity (10 <sup>-6</sup> m <sup>2</sup> /s)
0	999.87	1.787
5	999.94	1.519
10	999.69	1.307
20	998.19	1.004
30	995.61	0.801
100	958.39	0.294

even 5,400 times as large. Freezing only occurs at  $-2^\circ\text{C}$ .

## 4.2 Concentrations

All inorganic compounds are more or less soluble in water, just like many organic compounds. The solubility, however, is very different between distinct compounds (Table 6). Therefore, the concentrations (see frame next page) in water vary significantly between different compounds. To illustrate this, Table 7 shows the concentrations for different compounds present in water of a normal composition in an Olympic pool of 2,000 m<sup>3</sup>. The table shows that the masses of dissolved compounds ranges from 3 truckloads to a fraction of one grain. Investigating a poisonous compound with a concentration of  $1\mu\text{g/l}$  in drinking water is like searching for a single Chinese in China (1 in a billion = 1 ppb). Microbiological research is even on a smaller scale; a bacteria of  $1\mu\text{m}$  has a volume of 10-15 liter. Finding a single bacteria is like finding 1 part in a million billion parts. The concentrations shown by table 6 are all expressed in terms of mass per mass or volume of solution. There is another way of expressing concentration, often used when talking about water treatment, which is molarity. Molarity is defined by the number of moles of a constituent divided by the volume of the solution.

Table 6 - Solubility product of some relevant salts

Salt	$K_s$ (at $25^\circ\text{C}$ )
$\text{CaCO}_3$	$3.8 \cdot 10^{-9}$
$\text{Al(OH)}_3$	$2.0 \cdot 10^{-32}$
$\text{Ca(OH)}_2$	$4.7 \cdot 10^{-6}$
$\text{Fe(OH)}_3$	$2.6 \cdot 10^{-39}$
$\text{CaSO}_4$	$7.1 \cdot 10^{-5}$
$\text{FePO}_4$	$1.3 \cdot 10^{-22}$
$\text{FeS}$	$1.0 \cdot 10^{-19}$

Table 7 - Concentration of compounds in water

Type of compound	Typical concentration	Unit	Mass (kg) in Olympic pool of 2000 m <sup>3</sup>	
Sea salt	36	g/l	72,000	3 truckloads
Sludge	10 (1%)	g/kg	20,000	1 truckload
Dissolved material	1,500	mg/l	3,000	1 van load
Nitrate	50	mg/l	100	2 barrels
Toxin (light)	10	µg/l	0.02	1 teaspoon
Toxin (heavy)	0.1	µg/l	0.0002	1 grain
Endocrine disrupter	1	ng/l	0.000002	1/100 grain

A concentration of 1 mol/L can also be denoted as "1 molar" (1M).

### 4.3 Ions

When dissolving compounds in water, most of them dissociate into separate ions. In natural water, significant concentrations of the following ions are present:

- cations: Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>, and in smaller amounts of Fe<sup>2+</sup>, Mn<sup>2+</sup> and NH<sub>4</sub><sup>+</sup>

- anions: Cl<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>

When more than one compound has dissolved in water, it is typically not possible to trace the origin of the mix. Has the sodium originated from NaCl or from Na<sub>2</sub>SO<sub>4</sub>, and has the sulphate originated from MgSO<sub>4</sub> or from Na<sub>2</sub>SO<sub>4</sub>? The sum of the valence concentration of the cations is equal to that of the anions, because water is electrically neutral. Using this information one can either check a water analysis or compute an unknown component using an ion balance. Every ion has a specific conductivity, which makes it possible to compute the electric

#### Lime

The word lime is used for various chemical substances that have calcium in them.

The exact reference being made is mostly dependent on the person or his occupation.

Some examples of the meaning of lime(stone):

- drinking water consumers and other laypeople often mean calcium (there is much limestone in the water), but also calcium carbonate (limestone scaling in the washing machine)
- geologists use the word for limestone, which mainly consists of calcium carbonate (dripstone caves are present in limestone areas)
- chemists often mean the base compounds CaO and Ca(OH)<sub>2</sub> (we use both quick and slaked lime)
- civil engineers use the word for all compounds containing calcium (in concrete, there is both free lime (CaO / Ca(OH)<sub>2</sub>) and bonded lime (calcium silicates, calcium carbonates, etc.)
- linguists mean 'the carbonic acid of the calcium metal', or 'mortar' or 'plaster' or 'stone', consisting mainly of limestone

Due to these irregularities, the single word lime(stone) should be avoided.

In compound words or in sentences the meaning can be made clear, like in:

- limestone aggressive      able to dissolve CaCO<sub>3</sub>
- limestone precipitate      able to precipitate CaCO<sub>3</sub>
- limestone scale              CaCO<sub>3</sub> deposit due to increasing temperatures
- limestone water              milky mixture of water and Ca(OH)<sub>2</sub> (mostly totally dissolved)
- limestone suspense          milky mixture of water and Ca(OH)<sub>2</sub> (mostly not dissolved)
- limestone                      limestone
- chalk oven                      oven for heating (burning) limestone or chalk (for products like CaO).

conductivity from the concentrations. A single concentration could also be computed from the known conductivity in reverse.

#### 4.4 Gases

Gases can dissolve in water. In a condition of free exchange between a liquid and a gas, there will be an equilibrium state for the concentrations of the gas according to Henry's Law:

$$H = C_w / C_g$$

in which:

$c_w$  = concentration of volatile matter in liquid (mol/m<sup>3</sup>)

$c_g$  = concentration of volatile matter in gas (mol/m<sup>3</sup>)

H = distribution coefficient of volatile matter (-)

Henry's Law shows that there is a single defined relationship between the concentrations of volatile compounds in gas and fluid states.

Different compounds have different solubilities, which are temperature dependent.

Table 8 shows the H values for solubility in water at different temperatures. Gases having a low H value are difficult to dissolve in water; gases having high H value dissolve easily. Carbon dioxide is about 30 times as easy to dissolve as oxygen, which in its turn is twice as easy to dissolve as nitrogen. The solubility of methane is comparable to that of oxygen.

The concentration of a volatile matter in the gas state is computed using the general gas law ( $pV = nRT$ ), which can be formulated as:

$$C_g = P_a / RT$$

in which:

$p_a$  = partial pressure of volatile matter in gas state (Pa)

R = universal gas constant = 8.3143 (J/mol/K) or (Pa m<sup>3</sup>/mol/K)

T = temperature (K)

In a pure gas the partial pressure equals the true pressure. Based on the gas law, a pure gas at 0°C and 101,325 Pa has a concentration of 44.6 mol/m<sup>3</sup> (1 mol in 22.4 l).

The partial pressure of a gas can be computed by multiplying the molar fraction (which equals the volume fraction) by the pressure.

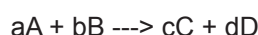
At sea level, air contains 78% nitrogen, 21% oxygen, 1% argon and 0.032% carbon dioxide. The volume fractions of the other gases (methane, hydrogen sulfide) are even lower. From this information one can compute that water, when it is in equilibrium with air at 10°C and 1 bar, contains 11.9 mg/l of oxygen (O<sub>2</sub>), 17.9 mg/l of nitrogen (N<sub>2</sub>) and 0.75 mg/l of carbon dioxide (CO<sub>2</sub>).

#### 4.5 Chemical reactions in water

The chemical equilibrium of a chemical reaction (transformation of reagents in products and vice-versa) is the state where the relative concentrations of both, reagents and products, are not changed. This means that any chemical reaction is characterized by species transformation rates that keep constant in the equilibrium, which is characterized as:

$$d/dt (\text{reagents}) = d/dt (\text{products})$$

The equilibrium is also characterized as



in which

A and B are the concentration of the reagents

Table 8 - Distribution coefficient H for the solubility in water

Compound		Distribution coefficient H		
		0°C	10°C	20°C
Nitrogen	N <sub>2</sub>	0.023	0.019	0.016
Oxygen	O <sub>2</sub>	0.049	0.041	0.033
Methane	CH <sub>4</sub>	0.055	0.043	0.034
Carbon dioxide	CO <sub>2</sub>	1.71	1.23	0.942
Hydrogen sulfide	H <sub>2</sub> S	4.69	3.65	2.87
Ozone	O <sub>3</sub>	0.64	0.54	0.39

---

C and D are the concentration of the products  
a, b, c and d are the stoichiometric coefficients of  
the reaction

The equilibrium constant is defined as

$$K_{eq} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

and it has the following properties:

1. It is constant for a certain constant temperature
2. Its equation does not include reagents or products that are in the solid state neither water

#### 4.5.1 Acid-base reactions

Acid–base reactions are common in water treatment, and pH has a significant effect on the chemical species present in water and on the efficiency of many treatment processes

##### Ionization of water

One of the most important chemical properties of water is that it can be both an acid and a base, because water ionizes into  $H^+$  and  $OH^-$  ions. The  $H^+$  ions associate with a water molecule into  $H_3O^+$ . In practice,  $H_3O^+$  and  $H^+$  are considered equal and used as equivalents.

These ions are formed at extremely high speeds and, at the same speed, they form water again. Normally, the number of ions at a certain moment is very low.

The ionization is an equilibrium reaction, for which an equilibrium constant can be determined. Because the concentration of  $H_2O$  is almost constant (55.6 mol/l), the equilibrium equation for water can be given as:

$$K_w = [H^+] \cdot [OH^-]$$

in which

$$K_w = \text{ion product of water} \\ = 1.0 \cdot 10^{-14} \text{ mol}^2/\text{l}^2 \text{ at } 25^\circ\text{C}$$

$$[H^+] = \text{concentration } H^+ \text{ ions (mol/l)}$$

$$[OH^-] = \text{concentration } OH^- \text{ ions (mol/l)}$$

For a neutral solution it holds (at  $25^\circ\text{C}$ ) that:

$$[H^+] = [OH^-] = 1.0 \cdot 10^{-7} \text{ mol/l} = 0.0001 \text{ mmol/l.}$$

This proves that there is a very small number of ions.

pH

The concentration  $[H^+]$  is usually denoted as the negative logarithm pH:

$$\text{pH} = -\log [H^+]$$

$$\text{pOH} = -\log [OH^-]$$

$$\text{pH} + \text{pOH} = 14.0 \text{ (at } 25^\circ\text{C)}$$

A neutral solution has a pH value of 7.0 at a temperature of  $25^\circ\text{C}$ . A lower pH, meaning a higher concentration of  $H^+$  ions, indicates an acid solution. A higher pH indicates that a solution is basic. By adding 0.1 mmol/l  $H^+$  the pH value falls to 4. Adding the same amount of  $OH^-$  would increase the pH to 10. Small amounts of acids and bases can have a large impact if there are no other reagents.

##### Dissociation of carbon dioxide

The most important acid-base reaction in water is related to the dissociation of  $CO_2$ .

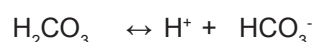
The dissociation of  $CO_2$  in water results on the formation of species that on one hand change the pH (due to the formation of  $H_3O^+$  ions) and on the other hand react with different species containing the carbonate ion (Such as  $CaCO_3$  present in supply pipelines and  $MgCO_3$ ), with consequences for the water properties.

$CO_2$  reacts with water:



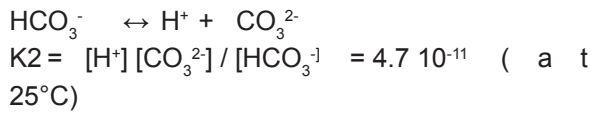
Though this reaction requires some time (a few seconds under normal conditions), the transformation is almost complete. In practice,  $CO_2$  and  $H_2CO_3$  are considered identical and are used as equivalents.

The dissociation continues from  $H_2CO_3$  to bicarbonate according to the following equilibrium reactions:





$$K1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 4.5 \cdot 10^{-7} \text{ (at } 25^\circ\text{C)}$$



From the equilibrium formulas it can be calculated which ionic forms of  $CO_2$  are present at a certain pH value.

For this purpose it is convenient to rewrite the formulas in the pK form ( $pK = -\log K$ ):

$$pK1 = pH + \log \left\{ \frac{[H_2CO_3]}{[HCO_3^-]} \right\} = 6.35 \text{ (at } 25^\circ\text{C)}$$

$$pK2 = pH + \log \left\{ \frac{[HCO_3^-]}{[CO_3^{2-}]} \right\} = 10.33 \text{ (at } 25^\circ\text{C)}$$

When the concentrations in the logarithmic part are equal, the ratio in that part equals 1 and, because  $\log 1 = 0$ , it holds then that  $pH = pK$ .

Therefore, at a pH value of 6.35,  $[H_2CO_3]$  equals  $[HCO_3^-]$ . For every higher pH unit, the ratio will be a factor 10 lower.

When  $pH = 10.33$ ,  $[HCO_3^-]$  equals  $[CO_3^{2-}]$ .

For a pH value lower than 8.3, the percentage of  $CO_3^{2-}$  is below 1%.

A certain pH is linked to a certain ratio between the reaction products, as can be seen in Figure 13.

Because of the  $HCO_3^-$  the pH value will change only slightly when adding an acid or a base. Acids and bases will be used by the transformation to  $CO_2$  or  $CO_3^{2-}$ . The buffer capacity indicates the amount of acid or base that is required for a pH change (mmol/l/pH).

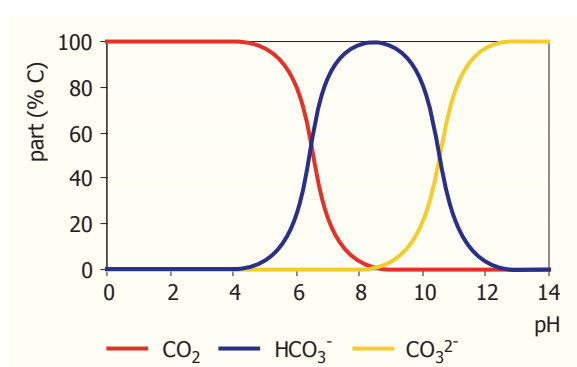


Figure 13 - Relationship between pH,  $CO_2$ ,  $HCO_3^-$  and  $CO_3^{2-}$

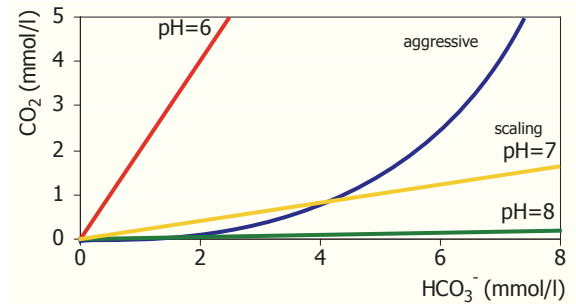


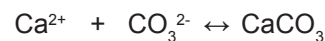
Figure 14 - Tillmans' diagram and different iso pH-lines

The  $H_2CO_3$  concentration in water is determined by adding a strong base which transforms all  $CO_2$  into  $HCO_3^-$ . At a pH value of 8.3 this transformation is almost complete.

The bicarbonate concentration in water is determined by adding a strong acid to water, which will transform all  $HCO_3^-$  into  $CO_2$ . At a pH value of 4.4 this transformation is almost complete.

#### 4.5.2 Calcium carbonate equilibrium in water

Calcium carbonate is a compound that is difficult to dissolve in water:



From a chemical perspective, this is a precipitation reaction, but in natural water also acid-base reactions with carbonic acid are involved. The solubility of calcium carbonate is given by:

$$Ks = [Ca^{2+}][CO_3^{2-}] = 3.8 \cdot 10^{-9} = 10^{-8.42} \text{ (at } T = 25^\circ\text{C)}$$

This means that the maximum concentration of  $Ca^{2+}$  that can be dissolved in water is 2.5 mg/L, since:

$$[Ca^{2+}][CO_3^{2-}] = 3.8 \cdot 10^{-9} \text{ and } [Ca^{2+}] = [CO_3^{2-}] \text{ so}$$

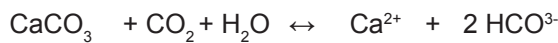
$$x^2 = (3.8 \cdot 10^{-9}) \Leftrightarrow x = (3.8 \cdot 10^{-9})^{(1/2)} = 6.2 \cdot 10^{-5} \text{ mol/L}$$

$$M(Ca) = 40,078 \text{ g/mol, so}$$

$$(6.2 \cdot 10^{-5} \text{ mol/L}) \cdot (40,078 \text{ g/mol}) = 0,0025 \text{ g/L} = 2,5 \text{ mg/L}$$

However, when  $\text{CO}_3^{2-}$  is removed from the water by some acid, the water can dissolve much larger amounts of  $\text{CaCO}_3$  and the hardness of the water will increase.

In nature, calcium enters the water because the calcium carbonate in the soil reacts with the  $\text{CO}_2$  from the water:



For this equilibrium reaction it holds that (at  $T = 25^\circ\text{C}$ ):

$$K = \frac{[\text{Ca}^{2+}] [\text{HCO}_3^-]^2}{[\text{CO}_2]} = 3.6 \times 10^{-5} = 10^{-4.44}$$

$$= K_s K_1 / K_2 = 10^{-(8.42 + 6.35 - 10.33)}$$

From the equilibrium above, when all calcium in the water has originated from calcium carbonate (and not from  $\text{CaSO}_4$  or  $\text{CaCl}_2$ ), it holds that  $[\text{Ca}^{2+}] = [\text{HCO}_3^-] / 2$ . Therefore, a third power relationship between  $\text{CO}_2$  and  $\text{HCO}_3^-$  holds for this equilibrium. The graphic presentation of this calcium carbonate (limestone) equilibrium is known as Tillmans' diagram (Figure 14).

Above the equilibrium line, the water is aggressive to limestone (i.e., dissolves limestone), below it limestone will precipitate. At higher temperatures the curve will shift upwards. The water that was in equilibrium will now be limestone precipitating, as is seen in the formation of  $\text{CaCO}_3$  deposits (scaling) in heating installations.

Aggressive water needs to be alkalized by removal of  $\text{CO}_2$ . This can be done by gas transfer (shifting along a vertical line in Figure 14, meaning a decrease of  $\text{CO}_2$ ), by adding a base (shifting under a 1:1 slope, meaning a decrease of  $\text{CO}_2$  and an increase of  $\text{HCO}_3^-$ ) or by reaction with  $\text{CaCO}_3$  with marble filtration (shifting under a 2:1 slope, meaning a decrease of  $\text{CO}_2$  and a double increase of  $\text{HCO}_3^-$ ).

In limestone-precipitating water there can be a precipitation of  $\text{CaCO}_3$  (shift under a 2:1 slope).

Table 11 - Calcium carbonate equilibrium constants (at  $\text{pK} = -\log K$ , with ion strength = 0)

	pK		
	10°C	25°C	100°C
$K_s$	8.36	8.42	9.20
$K_1$	6.46	6.35	6.45
$K_2$	10.49	10.33	10.16
$K_w$	14.53	14.00	11.27

The equilibrium constants for the calcium carbonate are given in table 9

### Saturation index SI

The degree of over- or under-saturation of calcium carbonate is indicated with the saturation index (SI).

From the equilibrium reaction it can be derived that:

$$\text{SI} = \log \left( \frac{[\text{Ca}^{2+}] [\text{CO}_3^{2-}]}{K_s} \right) = \text{pH} - \text{pH}_s$$

Here, the  $\text{pH}_s$  is the equilibrium pH value of water, with the same  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  concentrations:

$$\text{pH}_s = \text{pK}_2 - \text{pK}_s - \log \left( [\text{Ca}^{2+}] [\text{HCO}_3^-] \right)$$

Water having a positive SI is limestone precipitating, water with a negative SI is limestone aggressive.

### Conditioning

It is preferable that drinking water be slightly limestone precipitating. This will prevent cement-bound materials (concrete, asbestos cement) from corroding. Corrosion of these materials is caused by the dissolution of lime ( $\text{CaO}$ ) from the cement. By a limited precipitation of  $\text{CaCO}_3$  on metal pipe materials, the dissolution of metals like copper, lead, tin and zinc is prevented or reduced.

Hardness is defined as the sum of the concentrations of calcium and magnesium. The hardness of water occurs because the carbon dioxide in water dissolves the calcium carbonate and magnesium carbonate which are present in the ground.

Several units for hardness are used (mmol/l, German hardness degrees, French hardness degrees, American ppm  $\text{CaCO}_3$ ).

Soft water is preferable (total hardness lower than 1.0 - 1.5 mmol/l). Soft water is more pleasant to use (no film on tea, no unpleasant feeling when showering because of higher soap binding, no precipitation or scale in the washing machine, boiler or heater). In natural water the magnesium concentration is almost always limited (<0.5 mmol/l), making the calcium concentration especially important. When softening water in drinking water production plants, mainly the calcium concentration is reduced. At the same time  $\text{HCO}_3^-$  concentration should not be reduced too much. The  $\text{HCO}_3^-$  causes a stable water quality (buffer capacity).

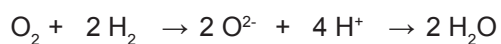
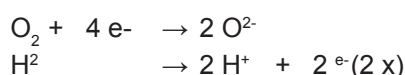
Because of the low hardness, the equilibrium pH value is relatively high (8.0 - 8.3). This increased pH value causes a lower copper and lead solvency of the water.

Besides being advantageous for human health, this is also advantageous for the environment (fewer heavy metals). Because of a lower hardness, fewer environmentally unfriendly phosphates are required in detergents. Phosphates are used in detergents to prevent the precipitation of  $\text{CaCO}_3$  on clothing and in washing machines.

Because of environmental and health advantages, drinking water is softened in The Netherlands. This central softening is also economically attractive to consumers (less use of soap, lower maintenance costs for hot water installations, no private environmentally unfriendly softening installation required).

### 4.5.3 Redox reactions

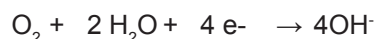
Water can be formed from the reaction of hydrogen and oxygen. In this reaction, oxygen is the oxidant (electron absorber) and hydrogen is the reductant (electron supplier). Such redox reactions are presented in the form of two half-reactions, from which the total reaction can be added:



This reaction can also be reversed under impact of electrical energy, transforming the water into oxygen and hydrogen again.

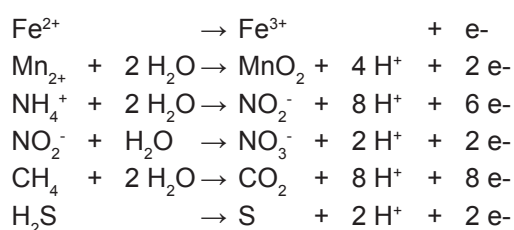
### Oxidation with oxygen in water

Also in water, oxygen is an important oxidant:



This oxidation reaction occurs when treating anaerobic groundwater. In this water several compounds are dissolved from the soil, like iron, manganese, ammonium, methane and hydrogen sulfide.

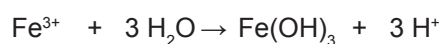
Oxidizing these compounds occurs according to the following scheme:



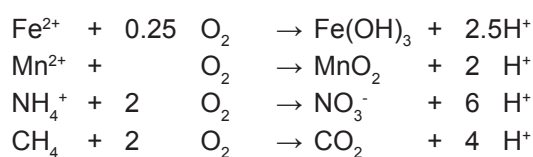
The extent to which the oxidation reactions above will occur depends on the standard electron potential of the reaction. There are reactions that will start spontaneously (Fe) or be influenced by some catalyst (Mn), or be influenced by bacteria ( $\text{NH}_4$ ,  $\text{NO}_2$ ,  $\text{CH}_4$ ,  $\text{H}_2\text{S}$ ).

The redox equation for each compound can be derived from the electron balance.

For the oxidation of iron it needs to be noted that, in order to remove the formed Fe(III), a precipitation reaction to brown iron hydroxide is required:



The added reactions, leaving out  $\text{H}_2\text{O}$  itself, are then:



The reaction equations show a high oxygen demand for ammonium and methane. They also

show that all named oxidation reactions are more or less acid-forming. This acid will react with  $\text{HCO}_3^-$  in water, forming  $\text{CO}_2$ .

## 5. Harmful compounds and organisms in drinking water

Some compounds in water are detrimental to human health.

### From threshold values to drinking water standards

For a number of compounds it is assumed that up to a certain concentration in the water there is no harmful effect to health, not even in the case of lifelong exposure. This is the threshold value (also referred to as NOAEL (No Observed Adverse Effect Level) (Figure 15).

The threshold value (NOAEL) is determined from animal tests, and needs to be extrapolated from animals to humans. This is done by dividing the animal NOAEL by a safety factor of 10 to 10,000, depending on the type of study, animal and effect. The tolerable daily intake (TDI) is calculated by multiplying safety-corrected NOAEL values by the average weight of some person (60 kg).

Drinking water is not the only source of certain compounds. Man also absorbs compounds from food and inhaled air.

From the TDI for some compound the standard value (maximum allowable concentration) for drinking water is calculated, assuming a certain

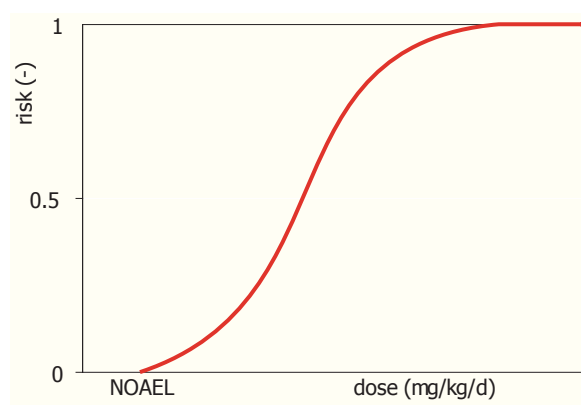


Figure 15 - Toxic compounds with threshold values

Table 10 - Estimated actual share of drinking water in the TDI (norm is 10%) and total daily intake

	The actual share in tolerable daily intake (%)	The acceptable share for drinking water of the total daily intake (%)
Arsenic	< 2	< 4
Cadmium	< 1	< 1
Lead	8	8
Nitrate	< 2	< 4
Copper	< 2	25
Nickel	1	4

accepted absorption from drinking water and the assumed drinking water consumption.

Mostly a maximum of 10% of the TDI is allowed to be absorbed via drinking water (Table 10).

The derivation of the water standard from NOAEL via TDI can be illustrated by the norm values for nickel. The NOAEL for nickel is 5 mg/kg/d. The extrapolation from animals to man is performed by using a safety margin of 1,000. The NOAEL for man is, therefore, 5  $\mu\text{g}/(\text{kg}\cdot\text{d})$ .

The TDI at which no harmful effects occur to man is 0.3 mg/d (the NOAEL multiplied by the average weight). The accepted share of drinking water for the TDI is 10% (about 10% of the daily nickel absorption comes from drinking water). The average amount of drinking water consumed per day is 2 liters. The norm value for nickel will be  $(0.3 / 2 \cdot 0.1 \cdot 1,000 =)$  0.015 mg/l. Rounded off, the standard is 20  $\mu\text{g}/\text{l}$ .

For some carcinogenic compounds a threshold value is defined, whereas for genotoxic-carcinogenic compounds, it is assumed that any concentration of it may have a harmful effect.

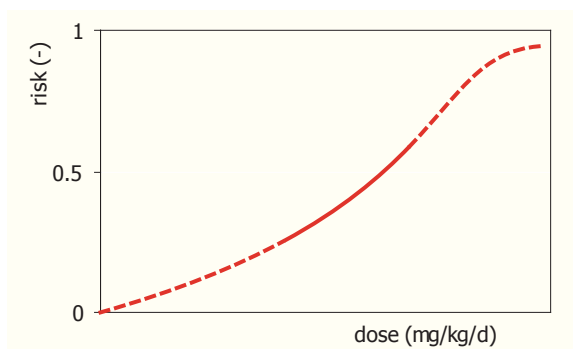


Figure 16 - Toxic compounds without threshold values

Every molecule of a genotoxic-carcinogenic could change a body cell into a cancer cell. The dose-effect relationship for these compounds is shown in Figure 16.

Water treatment cannot guarantee that such compounds are fully absent. In order to set standards for carcinogenic compounds, two approaches may be used:

- setting the standard at the level which is technically and economically feasible
- determining the acceptable risk and calculating the acceptable concentration from it

The acceptable risk is, for example, the chance for an individual to get cancer during his/her lifetime. The risk that is set is 1 in every 1,000,000 people, or a chance of  $1 \cdot 10^{-6}$ . This corresponds with a yearly risk of  $10^{-8}$  (assuming a lifetime of 100 years).

Every activity carries some risks. Of some risks we are conscious, of others we are not. Risks are subdivided into voluntary and involuntary risks. Voluntary risks are determined by people themselves. When riding a motorbike or smoking a cigarette, people can choose for themselves whether they take the risk or not.

Involuntary health risks are not chosen by the people themselves. For example, drinking water contains some health risk, however small, which needs to be accepted because one cannot live without water. The health risks from food are, in general, much higher than water because the relative intake of many compounds via food is much higher than the intake via drinking water. The voluntary acceptable risks are higher than the involuntary risks (Table 11).

Table 11 - Risks per activity

Activity	Risk of dying (per person per year)
Voluntary:	
- smoking	$5 \cdot 10^{-3}$
- riding a motorbike	$2 \cdot 10^{-3}$
- mountaineering	$4 \cdot 10^{-5}$
- plane crash	$2 \cdot 10^{-8}$
Involuntary:	
- drinking water per compound	$1 \cdot 10^{-8}$

The determination of involuntary acceptable risks is done by the government. In the Netherlands it was determined that for genotoxic compounds in drinking water the risk should not be above  $1.0 \cdot 10^{-6}$  per human life.

A few standards for drinking water are formulated on the basis of indicator organisms such as E. Coli (see 2.3 Compounds in water). With the absence of indicator organisms, it is assumed that other pathogenic microorganisms will not be present in the drinking water either.

Regarding chemical compounds, three elements are harmful in concentrations above 1 mg/l:

- nitrate (50 mg/l)
- copper (2 mg/l)
- fluoride (1 mg/l)

High nitrate concentrations can lead to methaemoglobinemia in small children ("blue babies disease").

High fluoride concentrations can lead to bone deformations (fluorosis).

High copper concentrations leads to digestive complaints.

Other chemical compounds can even be harmful in concentrations below 1 mg/l.

Arsenic causes the Blackfoot disease, mercury causes brain diseases, and aluminum is related to the early onset of Alzheimer's disease.

The health effects of the different compounds can be found in literature published by national governments, but also internationally by the World Health Organization (WHO) of the United Nations.

### Ethical levels

The standard of a certain compound is not always related to the health risks of that compound. A standard is sometimes based on summation parameters or on arbitrary standards for groups of compounds. For example, for pesticides there is a single ethical standard of  $0.1 \mu\text{g/l}$  in the European drinking water regulations. Within the group there is no differentiation for the different toxicities of the pesticides.

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Besides, standards are set for technical or aesthetic/organoleptic reasons for compounds which are not toxic but which may influence the flavour, colour and odour of the water.

### **Balancing the different health risks**

When a standard is exceeded, that does not mean that the water can no longer be drunk. First, because of the applied safety margins, and second, because the standards are not all toxicological, and exceeding them is often temporary.

A temporary high concentration of trihalomethanes (compounds which are produced during disinfection with chlorine) can be preferred over abandoning disinfection, because the latter may lead to infectious diseases.

## **6. Drinking water quality**

### **6.1 Framework for the regulations**

New European legislation needs to be translated into national law within a certain period. In the formulation and execution of this legislation, many governments and agencies have been involved.

#### **Water Framework Directive**

The European Water Framework Directive (December 2000) set a new framework for water management. The directive aims at improving the quality of water systems, and at making a sustainable use of water.

According to the Framework Directive, a reasonable amount of cost recovery for water services needs to be achieved, and the water price policy should stimulate efficient use of the available amounts of water. The principle that the polluter pays is one of the leading principles of the directive. This cost recovery, including external costs, is achieved by the water companies to a sufficient level.

The Framework Directive requires the formulation of a list of priority compounds, for which emissions into surface water should be reduced or stopped. It is important that those compounds which are problematic in drinking water production are included.

The Association of Dutch Water Companies (VEWIN) supplied data about the occurrence of pollutants in drinking water sources and they will, together with the European organization EUREAU, strive for a high priority of the compounds that are problematic.

#### **National government**

The national government creates the framework within which the water companies can produce good drinking water. In the Netherlands the Water Supply Act and the Decree on the Water Supply set the prerequisites that need to be fulfilled.

#### **Provincial government**

The policy, as it has been formulated by the central government, is elaborated into plans and regulations by provincial governments. For example, the provinces give substance to the measures that are written for the protection of groundwater. In this, they cooperate with the water companies. Also, the provinces hand out permits for the abstraction of groundwater.

#### **Water boards**

The water boards are, together with the Ministry, responsible for the quality and quantity of regional waters in the Netherlands. The water boards maintain the water level within their regions and, if necessary, they discharge water. Additionally, the water boards are responsible for wastewater treatment, checking the quality of surface water, and maintaining canals and city water.

#### **VROM-Inspection**

Water companies regularly take drinking water samples themselves in order to verify the quality of the product. The regional inspectors of the Ministry of Housing, Spatial Planning and the Environment (VROM), supervise the water companies, constantly scrutinizing the health effects, the hygiene, and the supply certainty of the Dutch drinking water.

#### **Water companies**

The water companies in the Netherlands provide a 24-hours-per-day supply of reliable water from the taps.

In case of problems they decide together with the VROM inspector whether the supply of drinking water should be continued. If continuation is impossible, some other supply must be found. The water companies, after all, guarantee continuous supply.

## 6.2 Drinking water quality according to legislation

The standards to which drinking water in the Netherlands should comply are registered in the Decree on Water Supply, which is an extension of the Water Supply Act. The Decree on Water Supply is regularly adapted to the most scientific insights and to developments in related legislation or European directives, such as EU 98-83-EC.

The Decree on Water Supply also regulates quality standards for surface water suitable for drinking water production.

Within the Decree on Water Supply, the following categories of parameters regarding drinking water can be distinguished (as previously mentioned in the chapter “drinking water technical setup”):

- public health (microbiological and chemical) parameters
- operational parameters
- organoleptic / aesthetic parameters
- signaling parameters

### Health-related, microbiological parameters

The microbiological parameters (Figure 17) having a health-related background are shown in Table 12. E(scherichia) coli was formerly measured as thermal tolerant bacteria of the coli group (44°C) and Enterococci were measured as faecal streptococci. Microorganisms are not allowed to be present in drinking water in such concentrations that may harm human health. For certain microorganisms like viruses and protozoa, (e.g., Cryptosporidium and Giardia), it is impossible to measure concentrations at the low level that is relevant for human health. Instead, the owner who uses surface water for drinking water production needs to formulate a risk analysis for the water based on measurements

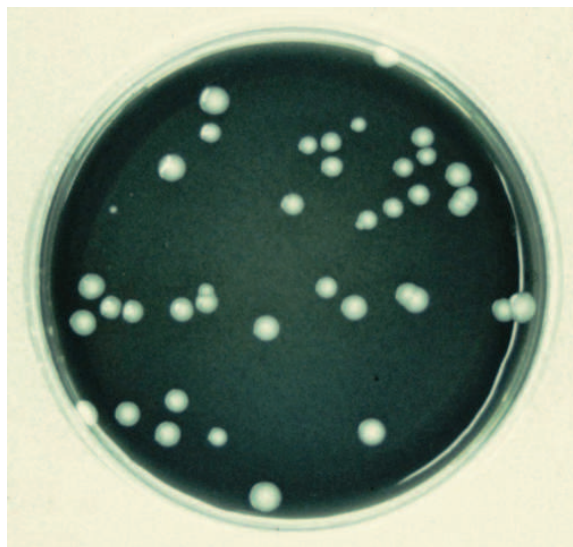


Figure 17 - Bacteria seen in a culture

of the relevant microorganisms in raw water and data concerning their removal in specific treatment processes, including soil passage in case of infiltration/recovery.

The microbiological parameters in drinking water are quite critical. Even a small contamination may lead to exceeding some standard. In that case, an emergency disinfection is applied and the consumers are advised to boil the water before using it.

### Health-related, chemical parameters

The chemical parameters having a health-related background are represented in Table 13. The table shows that for wider standards have been set disinfection by-products (bromate in the case of ozone, trihalomethanes in case of chlorination)

The relatively high values for cadmium and copper originate from a compromise between health

Table 12 - Health-related, microbiological parameters in the Degree on Water Supply

Parameter	Maximum Value	Unit
Cryptosporidium	1)	
Escherichia coli	0	CFU / 100 ml <sup>2)</sup>
Enterococci	0	CFU / 100 ml <sup>2)</sup>
(Enter) viruses	1)	
Giardia	1)	

1) Not present in the drinking water in such a concentration that it 's dangerous for the public health

2) CFU = colony forming units

Table 13 - Health-related, chemical parameters in Decree on Water Supply

Parameter	Maximum value	Unit	Remark
Acrylamide	0.10	µg/l	
Antimony	5.0	µg/l	
Arsenic	10	µg/l	
Benzene	1.0	µg/l	
Benzo(a)pyrene	0.010	µg/l	
Boron	0.5	mg/l	
Bromate	1.0	µg/l	With disinfection a maximum value of 5.0 µg/l is allowed (as 90 percentile value, with a maximum of 10 µg/l)
Cadmium	5.0	µg/l	
Chromium	50	µg/l	
Cyanides (total)	50	µg/l	
1,2 - Dichloorethane	3.0	µg/l	
Epichloorhydrine	0.10	µg/l	
Fluoride	1.1	mg/l	
Copper	2.0	mg/l	
Mercury	1.0	µg/l	
Lead	10	µg/l	Until 1-1-2006 the maximum is 25 µg/l
Nickel	20	µg/l	
Nitrate	50	mg/l	
Nitrite	0.1	mg/l	
Polycyclic Aromatic Hydrocarbons (PAHs) (sum)	0.10	µg/l	Sum of specified compounds with a higher concentration than the detection limit
Polychlorinated Biphenyls (PCBs) (individual)	0.10	µg/l	Per substance
PCBs (sum)	0.50	µg/l	Sum of the specified compounds with a concentration > 0.05 µg/l
Pesticides (individual)	0.10	µg/l	Per substance. For aldrin, dieldrin, heptachloor and heptachloorepoxide a maximum of 0.030 µg/l is stated
Pesticides (sum)	0.50	µg/l	Sum of the individual pesticides with a higher concentration than the detection limit
Selenium	10	µg/l	
Tetra- and tri-chloroethene(sum)	10	µg/l	
Trihalomethanes (sum)	25	µg/l	Sum of specified compounds (as 90 percentile with a maximum of 50) Until 1-1-2006 the maximum is 100 µg/l
Vinylchloride	0.50	µg/l	

effects and technical complexity (many copper pipes with cadmium-containing bronze connections).

#### Organoleptic/aesthetic parameters

The organoleptic or aesthetic parameters, shown on Table 14, concern the appeal of drinking water to the consumer, for drinking and for cleaning.

#### Operational parameters

The operational parameters are given in Table 15. Some operational parameters concern the danger of microbiological growth in the distribution network. This concerns both the organisms themselves and the temperature.

The minimum concentration of hydrogen carbonate should prevent small CO<sub>2</sub> formation, in case bio-

logical growth would lead to a large change in pH value (buffer capacity). The oxygen concentration should be high enough not to form anaerobic water, and the consequent negative effects like stench,

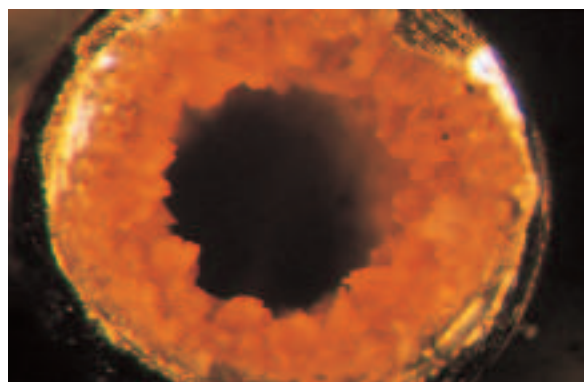


Figure 18 - Example of growth and scale in drinking water pipes



Table 14 - Organoleptic/aesthetic parameters in Decree on Water Supply

Parameter	Maximum value	Unit	Remark
Aluminum	200	µg/l	
Odor		-	Tolerable level for consumers and no abnormal changes
Color	20	mg/l Pt/Co	
Iron	200	µg/l	
Manganese	50	µg/l	
Sodium	150	mg/l	Yearly average with a max. of 200 mg/l
Taste		-	Tolerable level for consumers and no abnormal changes
Sulfate	150	mg/l	Water may not be aggressive
Turbidity	4 (taps) 1 (from pumping station)	FTU	FTU = formazine turbidity unit
Zinc	3.0	mg/l	After >16 hours of stagnation

etc. An example of growth and scale in drinking water pipes is shown in Figure 18.

Also the aggressiveness of the piping material should be limited (SI, pH, EC, chlorine).

The standards for SI, hardness and hydrogen carbonate are made quite strict (pH range between 7.6 and 8.5), which is advantageous for the metal dissolving capacity (copper, lead).

For hardness there is not only a minimum but also a maximum value. Hard water, actually, gives scale in the case of heating in laundry and heating installations. Besides, hard water leaves a visible film on tea and causes, by a chemical reaction with soap, a residue on the skin when showering.

To prevent households from softening the water themselves, a maximum hardness is included in the standards. Central softening is better for public health and for the economy than private softening.

#### Signalling parameters

Signalling parameters are intended to indicate possible contaminations.

When the standard value is exceeded, there is no direct risk for public health, but closer investigations need to be performed. This group of parameters is meant to safeguard the quality of the source. The signal parameters are given in Table 16.

Table 15 - Operational parameters in Decree on Water Supply

Parameter	Maximum value (unless stated otherwise)	Unit	Remark
Aeromonas (30°)	1,000	CFU/100 ml	CFU = colony forming unit
Ammonium	0.2	mg/l	
Bacteria of the coli group	0	CFU/100 ml	
Bacteriophages	-	PFU	PFU = plaque forming unit
Chloride	150	mg/l	
Clostridium perfringens (incl. spores)	0	CFU/100 ml	
DOC / TOC	-	mg/l	No abnormal changes
EC (bij 20°C)	125	mS/m	Water must be non-aggressive
Hardness (total)	> 1 and < 2.5 mmol	mmol/l	Total hardness to be calculated as an amount of mmol Ca <sup>2+</sup> and Mg <sup>2+</sup> /l. If softening or desalting is used then the 90 percentile value is applied.
Colony number at 22°C	100	CFU/ml	Geometric yearly average. No abnormal changes
Radio activity:			
- Total α	0.1	Bq/l	
- Total β	1	Bq/l	
- Tritium	100	Bq/l	
- Indicating dose (total)	0.10	mSv/j	
Saturation Index (SI)	> -0.2	SI	Water must be non-aggressive
Temperature	25	°C	Only for cold distributed drinking water
Hydrocarbonate	> 60	mg/l	
pH	> 7.0 and < 9.5	pH	Water must be non-aggressive
Oxygen	> 2	mg/l	

Table 16 - Signalling parameters in Decree on Water Supply

Parameter	Maximum value	Unit
AOX	-	µmol X/l
Aromatic amines	1 *	µg/l
(Chloor) fenolen	1 *	µg/l
Halogenated monocyclic carbons	1	µg/l
Halogenated aliphatic carbons	1	µg/l
Monocyclic carbons / aromatics	1	µg/l

\* If as metabolite of pesticides then 0.1 µg/l

### 6.3 Safeguarding drinking water quality

The Decree on Water Supply dictates how and when the quality of drinking water should be determined. It also determines the quality which should be safeguarded at the sources and during the treatment process.

Tables 17 and 18 show the safe guard parameters, measurement frequencies, and sample locations for the different parameter groups.

## 7. Water quality for other applications

There are other applications for water besides drinking. Every application has specific requirements for water quality, which can be indicated as rough requirements such as clean, soft, without salts, etc.. Table 19 shows some examples.

### Household water

Household water is used for flushing the toilet, watering the garden, washing the car, and in washing machines for clothing and dishes. Household water is generally not used for drinking water.

During the test projects that have been performed during the past few years in the Netherlands, how-

ever, it has been shown that cross-connections between drinking water and household water frequently occur. This is not only due to mistakes during construction, but also due to the use by the inhabitants (fiddling with pipes, using the garden hose for the children's bathtub, etc.). It is, therefore, necessary to make the household water ready for consumption. Although household water, it is not intended for long-time exposure; the risk of some acute microbiological contamination is not imaginary.

In principle it is possible to prevent such a microbiological contamination by applying chemical disinfection using chlorine. However, this leads to the formation of harmful by-products like trihalomethanes. The question arises as to whether the disadvantages of household water (costs, health risks, environment) are not larger than the intended advantages (savings on drinking water). These developments have led to very strict regulations for household water projects, which are nowadays discouraged by the Dutch government.

### Cooling water

In industry, much water is used as cooling water. Of course, the water temperature is important for this application. This makes groundwater attractive, because it has a constant temperature. However, obtaining a permit to use groundwater for this low-end application is almost impossible.

Cooling water is used in heat exchangers and piping systems. In these applications no scaling is allowed to occur and the materials used should not be affected. In order to limit the use of cooling water, often circulation cooling is chosen, meaning that a part of the water evaporates so that con-

Table 17 - Measurement frequencies for controlling and audits as stated in Decree on Water Supply

Daily amount of distributed and processed water within a delivery area in m <sup>3</sup>	Controlling Number of samples per year	Audit Number of samples per year
<100	2	1
100 - 1,000	4	1
1,000 - 10,000	4 + 3 for each 1,000 m <sup>3</sup> /d and a fraction of the total amount	1 + 1 for each 3,300 m <sup>3</sup> /d and a fraction of the total amount
10,000 - 100,000	4 + 3 for each 1,000 m <sup>3</sup> /d and a fraction of the total amount	3 + 1 for each 10,000 m <sup>3</sup> /d and a fraction of the total amount
>100,000	4 + 3 for each 1,000 m <sup>3</sup> /d and a fraction of the total amount	10 + 1 for each 25,000 m <sup>3</sup> /d and a fraction of the total amount

Table 18 - Controlling parameters in Decree on Water Supply

Parameter group	Sample point t <sup>1</sup>	Sample point p/t <sup>2</sup>
Microbiological parameters	Escherichia coli	-
Chemical parameters	Nitrit	-
Operational parameters	- Ammonium - Bacteria of the coli group - EC - Colony number at 22°C - pH	Clostridium perfringens
Organoleptic / esthetic parameters	- Odor - Color - Taste - Turbidity	Aluminum Iron
Signalling parameters	-	-

<sup>1</sup> t = at tap point for human consumption

<sup>2</sup> p/t = after last treatment step at treatment plant and at tap point for human consumption

centrations will increase. Nevertheless, pollution, scaling, and corrosion should remain limited.

The quality requirements for cooling water, therefore, are:

- low turbidity (pollution)
- sufficient oxygen concentration, good pH value and low electric conductivity (corrosion)
- low hardness and good pH value (scaling of CaCO<sub>3</sub>, CaSO<sub>4</sub>, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>)
- low silicate concentrations (scaling of SiO<sub>2</sub>)

#### Hot or cold flushing water

In industry, a large quantity of water is used as flushing water. Critical applications of this are found in the food industries (bottle flushing, cleaning of process installations). Less critical applications can be found everywhere (cleaning water for buildings). For good cleaning, warm or hot water is used almost exclusively.

Flushing water requires in the first instance, the same considerations as cooling water (no scaling and no corrosion). However, in the second instance also a low salt concentration is required,

as all remaining water will evaporate and visible salt residuals can otherwise be formed.

#### Boiler feed water

Boiler feed water is used for the production of steam, which means the water completely evaporates. In industry, considerable amounts of water are used for this purpose, despite reuse (boiler feed water for the production of boiler water, re-abstracted as condensate).

The quality requirements for boiler feed water depend on the operational pressure of the steam, the kind of steam boiler (large water storage or water pipe), and the possibility of condensate cleaning or reuse.

Typically, fully softened water is used for the production of low-pressure steam, and fully desalinated water is used for high-pressure steam.

#### Greenhouse water

Greenhouse water is applied in agriculture and horticulture. The quality of the water is important, because this water is used many times to save

Table 19 - Quality aspects for different usages

Usage	Specific goal	Aspect
Drinking water	- Household water - Drinking water	Clean, safe + healthy
Cool water	- Circulation - Open circulation	Cold, clean (contamination) + soft / low salt (scaling)
Rinse water	- Cold - Hot	Clean + soft (scaling)
Boiler feed water	- Low pressure - High pressure	Clean, soft + salt free (scaling)
Greenhouse water	- Circulation	Low salt (affecting plants)

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water overall, and to limit discharges of nutrients and pesticides.

Plants evaporate water, causing condensation of the circulating water and salt accumulation in the vegetation itself. The sensitivity for salt accumulation differs per type of vegetation.

Generally, a sodium concentration below 60 mg/l is desirable.