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Masterclass:

WATER POLLUTION

E-LIBRARY CONTENT

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Cm- Coulomb metre, SI unit of the electric dipole moment

cP- Centipoise, the unit of dynamic viscosity (absolute viscosity) ($1cP=10^{-3}$ Pa·s)

SDGs- Sustainable Development Goals

QWTs- Quality water targets

MACs- Maximum Allowable Concentrations

WHO- World Health Organization

CO_2- Carbon dioxide

CO_3^{2-}- Carbonate ion

HCO_3^-- Bicarbonate ion

OH^-- hydroxide ion

$CaCO_3$- calcium carbonate

BOD- Biochemical oxygen demand

COD- Chemical Oxygen Demand

DDT- Dichlorodiphenyltrichloroethane

NORM- Naturally occurring radioactive matter,

USA- The United States of America

LC_{50}- "Lethal concentration"- The concentration that causes death of 50% of the exposed population

1. INTRODUCTION

Water is a common name for liquid state of hydrogen oxide at standard ambient pressure and temperature. Its molecule, represented by chemical formula H_2O, consists of two atoms of hydrogen and one atom of oxygen. It is the only inorganic liquid that is colourless, odourless, and tasteless. Water is the most widespread liquid on Earth (71% of Earths' surface is covered by water (Mayer, 2004)) and it is the basis of life on Earth. There are several theories about water origin on Earth. The latest studies suggest that water on Earth came from co-called solar nebula, a cloud of gasses and dust that remained after Suns' formation and from the asteroids and meteors, that "bombarded" Earth during the early stage of its life as a planet (https://earthsky.org).

It is believed that life on Earth has originated in the aqueous solutions in oceans, and all living organisms depend on water, either on aqueous solutions (for instance blood or digestive juices) or on water as the essential part of metabolic processes. Besides that, form the beginning of mankind, water plays an important role in human life. It is used for drinking, in households for cooking, washing, and cleaning, and in various industries. It also plays an important role in transport of commodities and with time it has become a valuable commodity itself with an economic value, which will be even more emphasised in the future with growing problems of climate change.

From the antient times water is considered to be, along with air, earth and fire, one of the elementary matters. This was thought till the second half of the 18^{th} century when in 1781 British chemist Henry Cavendish discovered hydrogen or as he named it "inflammable air". He actually synthesised water from, when he sparked "dephlogisticated air" (oxygen) with "inflammable air", but this experiment was misinterpreted for several more years. French chemist Antoine Laurent de Lavoisier, known as the father of the modern chemistry, two years later proved that water is not elementary matter and that is actually a chemical compound made of oxygen and hydrogen. At the beginning of 19^{th} century (in 1804) in their joint scientific work, French chemist Joseph Louis Gay-Lussac and German natural scientist and explorer Friedrich Heinrich Alexander von Humboldt discovered that molecule of water is made of two parts of hydrogen and one part of oxygen (Mayer, 2004).

Water molecule is composed of two atoms of hydrogen which are linked to an atom of oxygen by a covalent bond. Water molecule is not linear but has a bent shape with a 104.5-degree angle between the two hydrogen atoms (Figure 1.) (Mayer, 2004; Zumdahl, 2021).

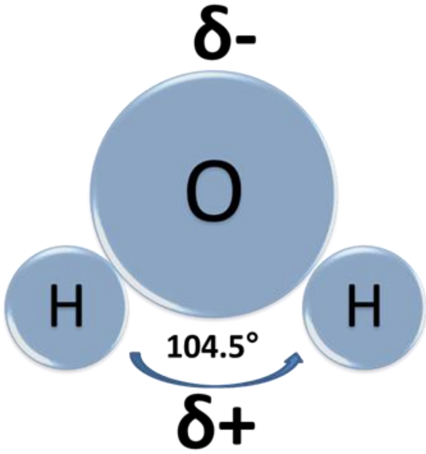


Figure 1 Water molecule

Water molecule is electrically neutral, but due to unsymmetrical structure and two pairs (4 electrons) of free electrons around oxygen, the positive and the negative charge are not evenly distributed which makes water a dipole with expressed negative charge around oxygen and expressed positive charge around hydrogen atoms (Figure 1). Dipole moment of water molecule is 6.14×10^{-30} Cm (Tedeschi, 1997). This makes water an universal solvent, but it is also the reason why water in nature gets easily polluted. Water has the ability to dissolve many organic and inorganic substances. In addition to polarity, water is a great solvent also because of its amphoteric characteristic. This means is that water can act as both an acid and base, which makes water a better solvent than most other polar molecules.

There is a link between hydrogen atom from one water molecule to oxygen atom from another water molecule forming so-called hydrogen bond. Namely, due to the expressed polarity, hydrogen atoms form one water molecule are attracted to the nonbonding electron pairs of oxygen atom in another water molecule. These hydrogen bonds are weaker than covalent bonds (Mayer, 2004; Tedeschi, 1997). Due to the hydrogen bonds, two, three, four or more water molecules form cyclically distributed supramolecule aggregates called water clusters. Due to weakness of hydrogen bonds, water clusters are not stable and are constantly forming and reforming.

There are three hydrogen isotopes- protium (^{1}H), deuterium (^{2}H) and tritium (^{3}H), as well as three oxygen isotopes, ^{16}O, ^{17}O and ^{18}O, so in theory there could be 18 types of water molecules. Deuterium was discovered by American scientist Harold Clayton Urey and his associates in 1931, for which Urey received the Nobel prize in 1934 (Hrvatska enciklopedija, 2021). Since there are extremely low quantities of isotopes ^{3}H, ^{17}O and ^{18}O, the most common form of water molecule is $^{1}H_2{}^{16}O$, even though some small quantities of $^{2}H_2{}^{16}O$ (D_2O, so-called heavy water) and $^{1}H^{2}H^{16}O$ ($HD^{16}O$) can be found (Mayer, 2004; Tedeschi, 1997).

The structure of water depends on its physical state. In nature, water occurs in three physical states- liquid (running water bodies, stagnant water bodies), solid (ice) and gaseous (water vapour) (Figure 2).

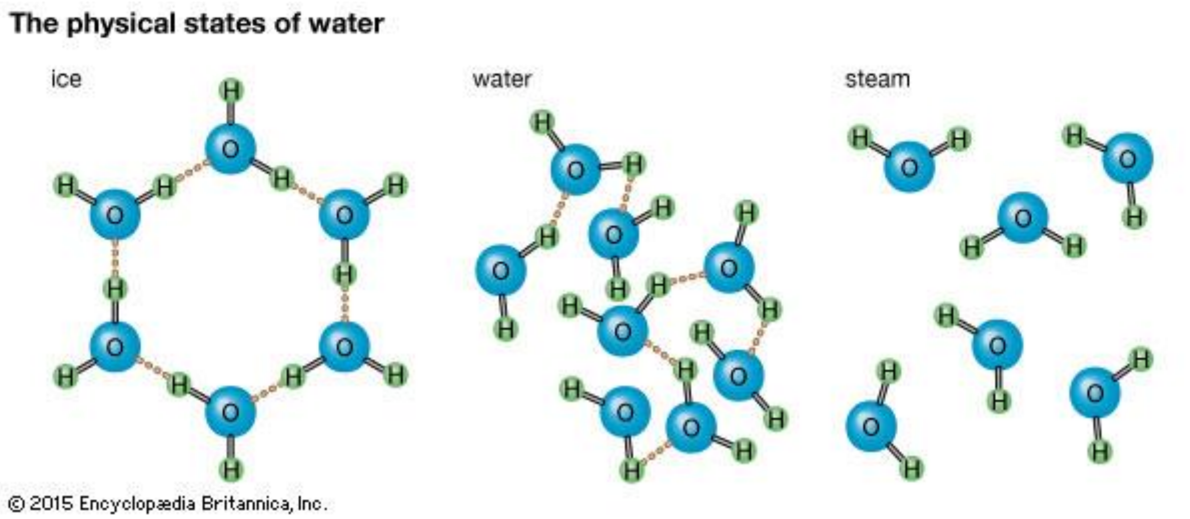


Figure 2 The physical states of water (Encyclopaedia Britannica, 2015)

In liquid and solid state, due to water polarity, beside mentioned hydrogen bonds between different water molecules, there are also electrostatic Van der Waals cohesion forces, which are weaker than hydrogen bonds, but still contribute to water cluster formation in liquid state. In gaseous state, water molecules, depending on molecules' kinetic energy (which again depends on water temperature and pressure), move freely and much faster than in liquid or solid state thus the cohesion forces between water molecules are not expressed.

Even though water seems to be a simple chemical compound built of only two elements, it has peculiar physical and chemical properties. It also shows various anomalies in its properties and behaviour (Figure 3). Physical properties of water are expressed by density, viscosity, surface tension, thermal, electrical, and optical properties. Chemical properties of water are solubility, oxidation-reduction reaction and ionization. Water has unusually high viscosity (0.89cP), surface tension (72.75×10^{-3} N/m), heat capacity, boiling and melting point and has unusually low compressibility, and low thermal expansivity (Mayer, 2004).

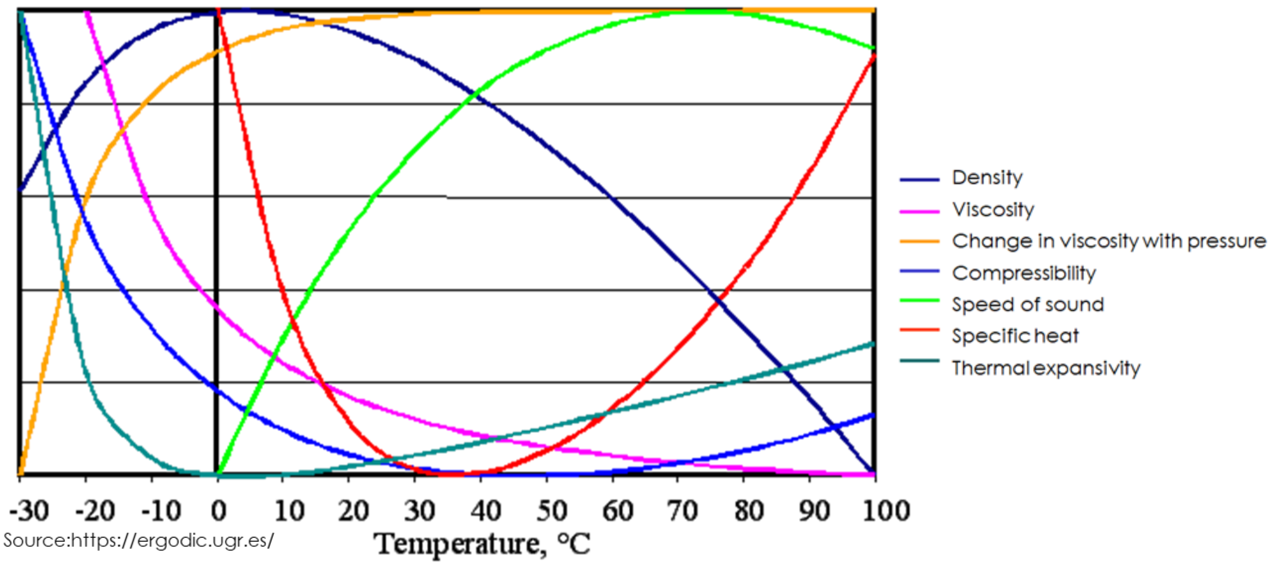


Figure 3 Some of the anomalies of water related to temperature (https://ergodic.ugr.es)

2. DISTRIBUTION OF WATER IN NATURE

Coming in different physical states and in different forms, water in nature is unevenly distributed between hydrosphere (99.29%), lithosphere (0.7%), atmosphere (0.001%), and biosphere (0.0001%) (Mayer, 2004) (Figures 4-6). The total amount of water on Earth equals about 1.386×10^{9} km^{3} (Balasubramanian, 2015) and most of it is in oceans and seas as salt water (97.40%) and only 2.6% appears as freshwater (Mayer, 2004) (Figure 4). The saline water is not suitable for direct consumption (drinking, cooking, irrigation, industrial processes etc.) so direct use of water is limited to only less than 3% of the total water amount on Earth.

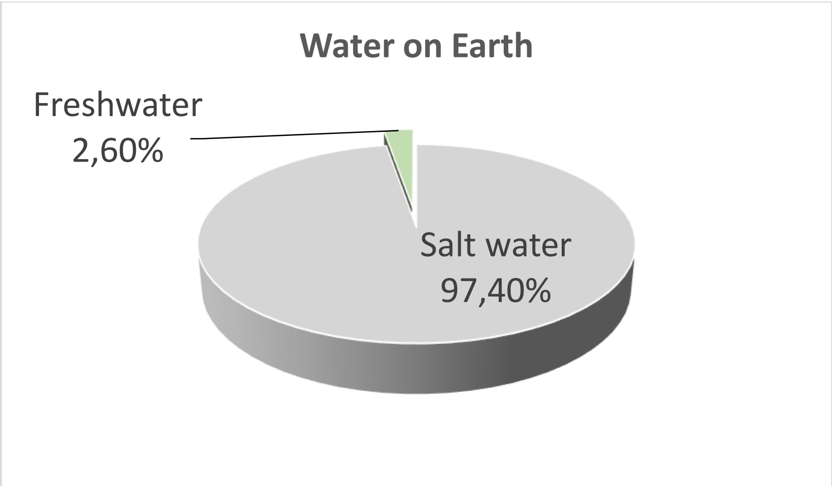


Figure 4 Distribution of water on Earth (adapted from Mayer, 2004)

Out of the 2.6% of freshwater, most of it is in solid state in form of glaciers and ice caps (68.70%). About 30.10% of it is below surface as groundwater and only 1.20% of it available as surface water and other freshwater (soil moisture and water vapour) (Mayer, 2004) (Figure 5).

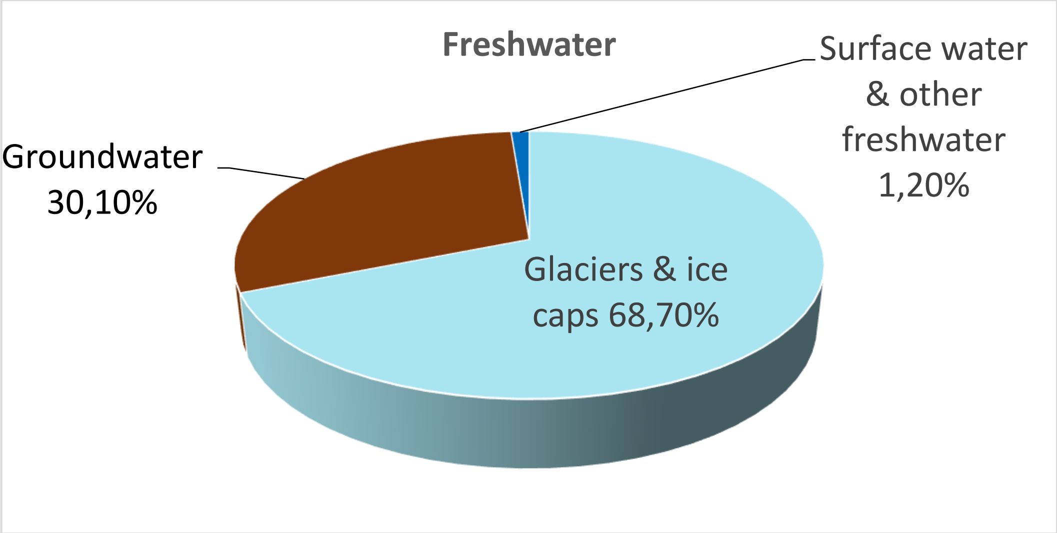


Figure 5 Distribution of freshwater on Earth (adapted from Mayer, 2004)

As mentioned, and as it could be seen from Figure 5, most of the surface water exist in form of ground ice and permafrost (almost 70%). The rest is shared by lakes (20.90%), soil moisture (3.80%), atmosphere (3.00%), swamps and marshes (2.60%), rivers (0.49%) and living beings (Mayer, 2004) (Figure 6).

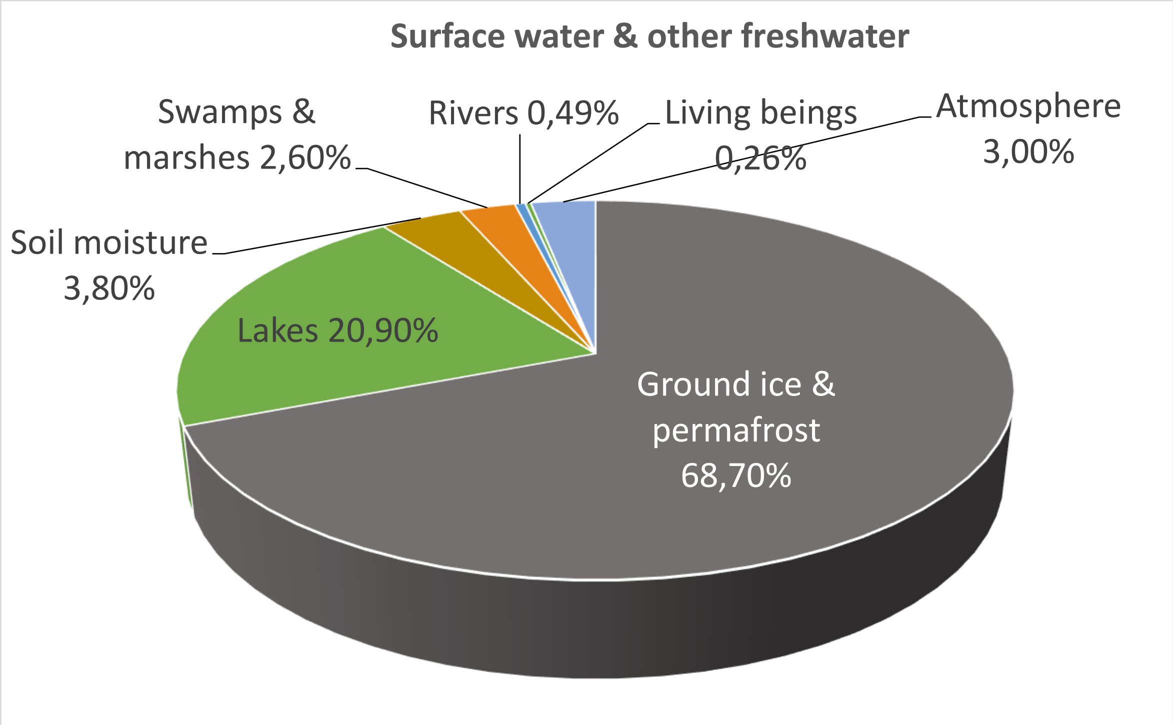


Figure 6 Distribution of surface and other freshwater on Earth (adapted from Mayer, 2004)

Although the total amount of water on Earth is constant, a certain amount of it is constantly circulating between hydrosphere, atmosphere, lithosphere, and biosphere having different retention time in a specific "sphere" ranging from several hours, like in case of living beings (biosphere) to several thousands of years, like in case of permafrost or polar ice caps (Figure 8). This constant circulation of water in nature is called hydrological cycle or water cycle (Figure 7). The hydrological cycle encompasses several simultaneous processes by which water mass is transported from oceans to the land (Balasubramanian, 2015):

- Precipitation;
- Infiltration;
- Surface runoff;
- Transpiration;
- Groundwater baseflow;
- Interception;
- Evaporation from free water surfaces;
- Condensation;
- Evapotranspiration.

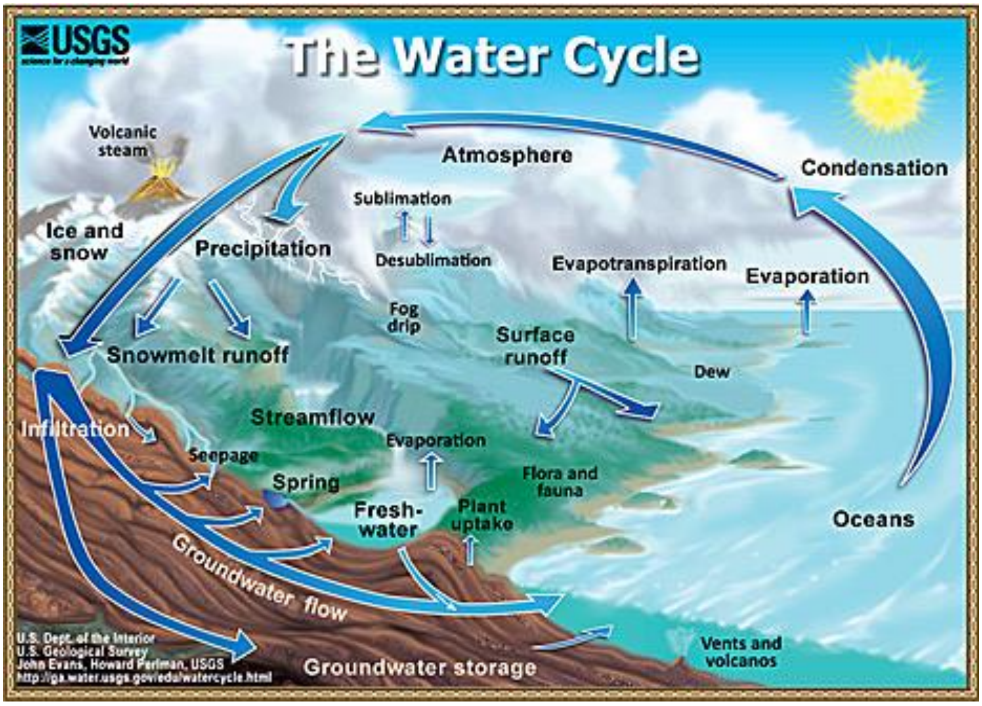


Figure 7 The hydrological cycle (https://water.usgs.gov)

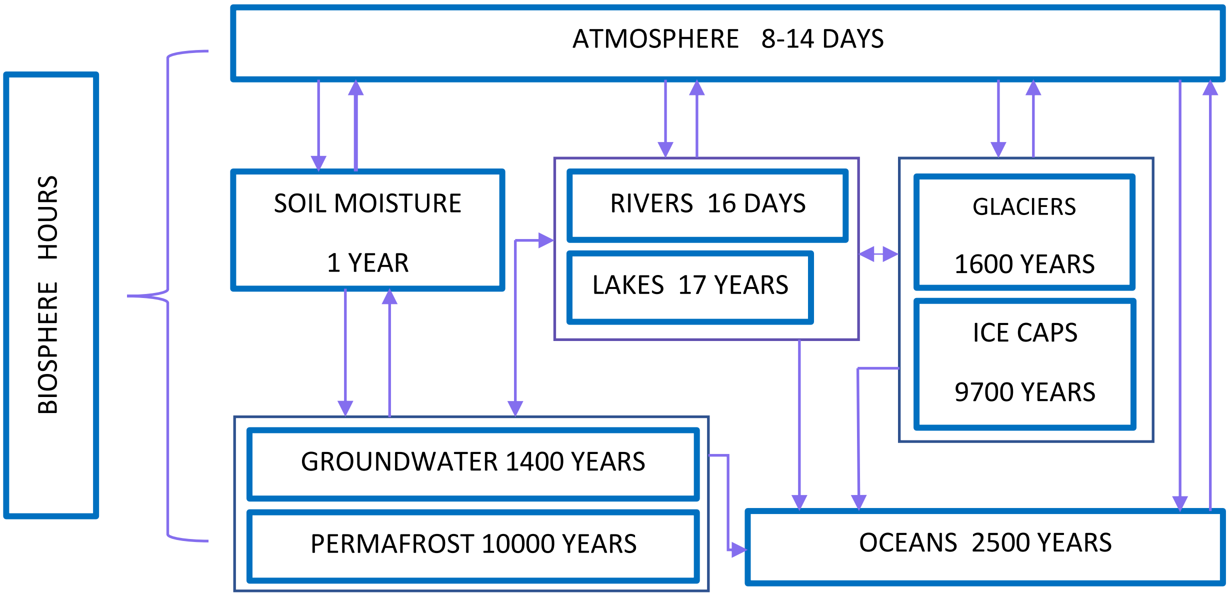


Figure 8 Water retention time during the water cycle (adopted form Orešić)

The retention time shown in Figure 8 represents the time necessary for the change of the total volume of water in specific water reservoir.

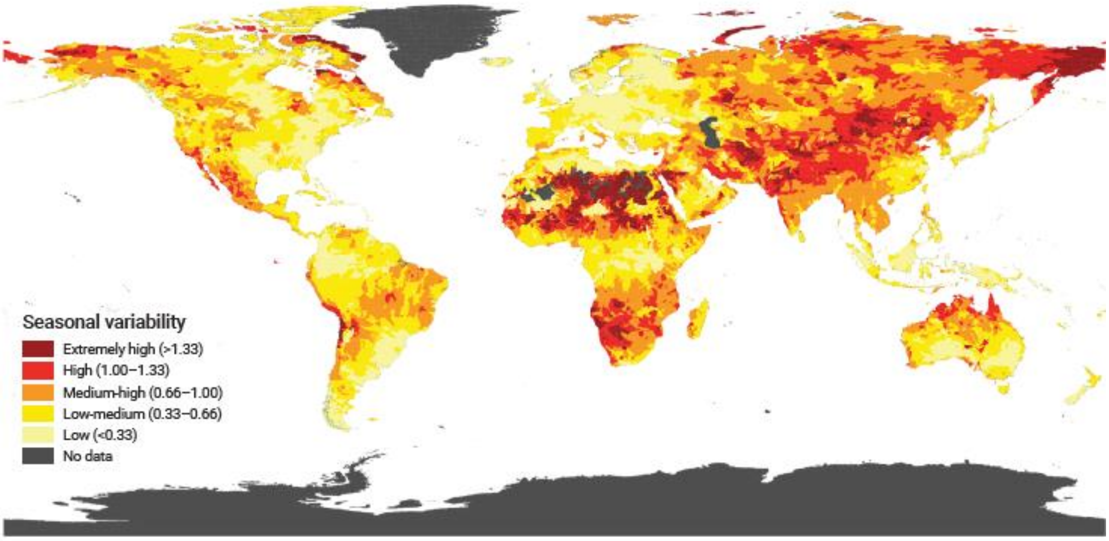
3. WATER RESOURCES AND SUSTAINABILITY

Freshwater became one of the strategic resources in the modern world. Regarding water resources, there are two pressing issues that emerged in the last 60 years. These are water pollution and water scarcity. Dealing with the mentioned issues requires comprehensive and sustainable approach to water resources management.

Due to water scarcity, securing sufficient water supply has become one of the major challenges in the 21st century. Beside the fact that water is the basis of life, water scarcity directly affects food and energy production as well as human health, all essential for humankind survival. Global freshwater resources are limited (less than 3% of total amount of water on Earth) and globally unevenly distributed. As a result of excessive withdrawals of both surface and groundwater, the available water resources are continuously declining and already some of worlds' regions are facing serious problems of water supply. This is further emphasised by the global climate change altering precipitation and evaporation patterns causing the dry areas to become more drier and rainfall seasons shorter in duration but more concentrated and extreme in terms of weather conditions. Due to the effects of climate change, water availability is becoming less predictable in many regions. Nowadays many regions of the world experience shifts in seasonal water availability throughout the year, since water scarcity manifests itself as seasonal phenomenon. Seasonal variability in available water supply is shown in Figure 9. The mentioned water scarcity is characterized as physical water scarcity. Around 1.6×10^9 people also face so-called economic water scarcity, which is the consequence of the lack of infrastructure to access water (UN, 2020).

Climate change also manifests itself as increased rate of bad weather conditions causing flooding, threatening freshwater water systems and infrastructure, and having both direct (loss of life, damage to buildings and infrastructure) and indirect (impact on human health, losses in productivity) impact on the society. Furthermore, since hydrological cycle is one of the factors defining the climate system, changes in hydrological cycle, caused by the climate change, further trigger the climate change and create one vicious cycle of cause and consequences. Projected water scarcity in 2025 is shown in Figure 10.

Climate change threatens not only the availability of water but also the quantity and quality of it. Affected by that are especially urban areas due to high population density and increasing urbanization. According to estimations, by the middle of 21st century, around 700×10^6 people living in around 600 cities will face an additional decline in freshwater availability of at least 10% due to the climate change. For some of the cities, for instance Cape Town and Melbourne, the decline is estimated to be more than 30%, and for Santiago the estimations go up to 50% decline (UN, 2020). Estimations of urban water supply decline are shown in Figure 11.



Note: Seasonal variability measures the average within-year variability of available water supply, including both renewable surface and groundwater supplies. Higher values indicate wider variations of available supply within a year.

Figure 9 Seasonal variability in available water supply (UN, 2020)

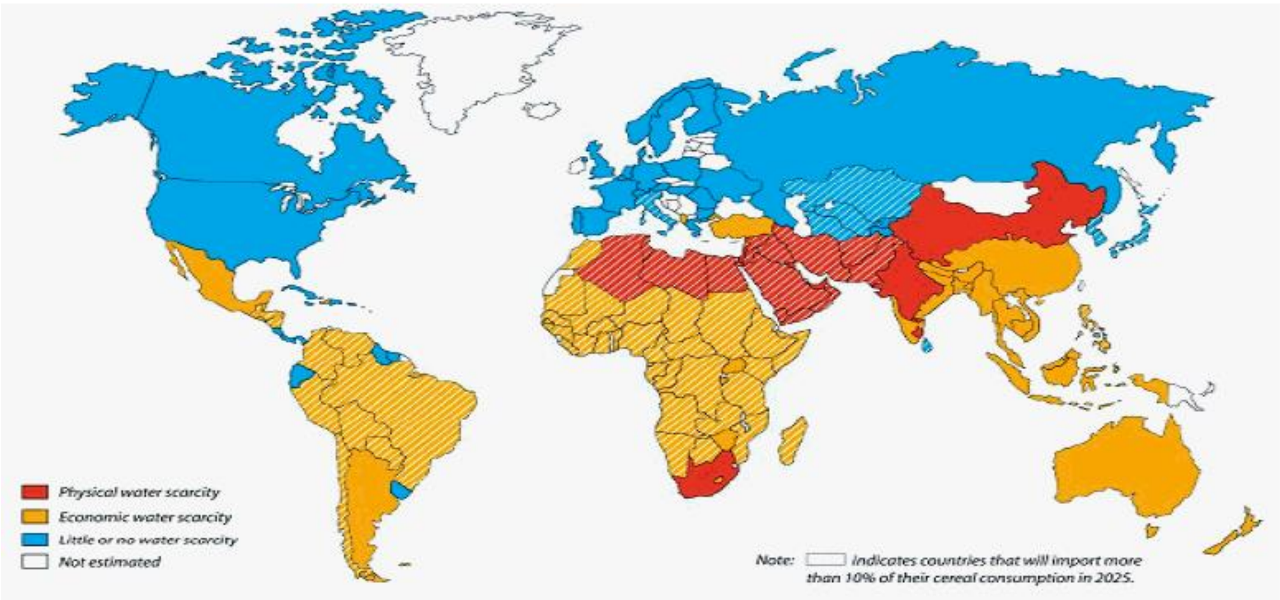


Figure 10 Projected water scarcity in 2025 (Hamdy, 2016)

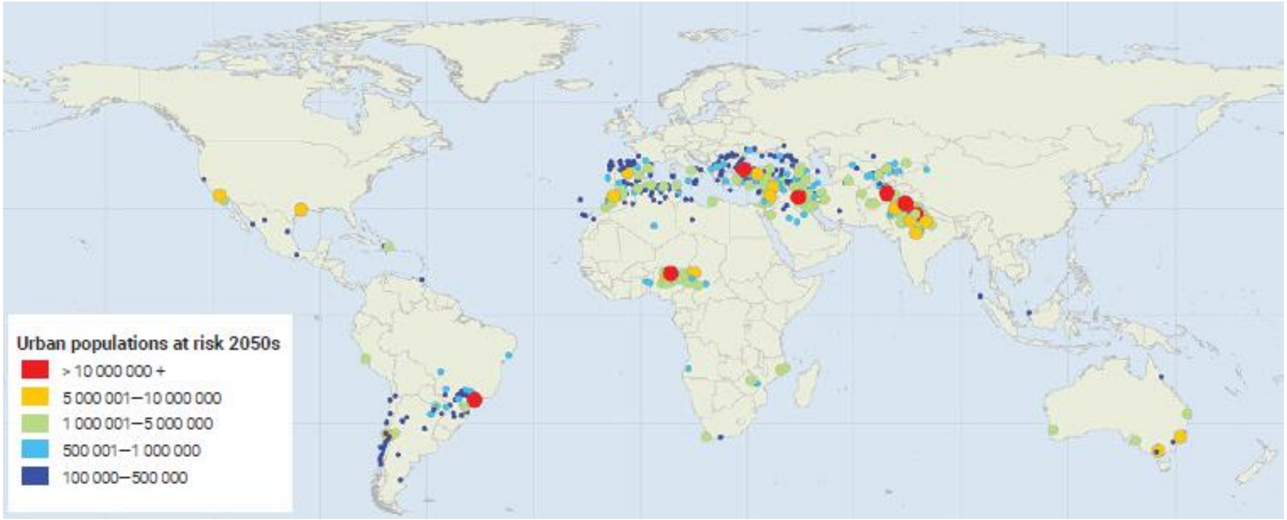


Figure 11 Estimations of decline in urban water availability by 2050 (UN, 2020)

The main drivers that caused water demand increase, which recorded the most significant change in the 20th century, are the increase in number of populations, industrial development, extensive irrigation agriculture, massive urbanization and economic development in general resulting with rising standards of living (Balasubramanian, 2015). In the last 100 years global water use has increased by a factor of six and it continues to grow at the rate of 1% per year (UN, 2020).

Over the last forty years, the emerging problems of water scarcity along with the problems of water pollution have made the international community to consider it, along with air pollution, as the most serious contemporary environmental problem and address it with appropriate international prevention and mitigation measures. Thus, water issues and challenges are taken into account in two major global agreement, the Paris Agreement on climate change and the Sendai Framework for Disaster Risk Reduction. They are also addressed in the international framework for the development, the 2030 Agenda for Sustainable Development adopted by the United Nations in 2015, which brought 17 Sustainable Development Goals (SDGs) with overall 169 targets to be achieved latest by 2030 (some of the sub-goals have even shorter period to be achieved like 2020 or 2025) (Figure 12) (https://sdgs.un.org/goals). The SDGs directly addressing the water issues are SDG 6 “Clean Water & Sanitation”, SDG 14 “Life Below Water” and SDG 15 “Life on Land”. Water is also indirectly addressed in others SDGs, like in SGD2 for producing food, SDG7 for energy production, supporting livelihoods (SDG 8) and industry (SDGs 9 and 12), providing sustainable and healthy environment to live (SDGs 1, 3 and 11), mitigation and adaption to climate change (SDG 13) and in building peaceful and inclusive societies (SDG 16).

Figure 12 The Sustainable Development Goals according to The 2030 Agenda for Sustainable Development (https://sdgs.un.org/goals)

Achieving the 2030 Agendas' goals most certainly implies sustainable water management, that is meeting the water needs of the present without compromising the ability of the future generations to meet their own needs. This requires multidisciplinary approach in which environmental, economical, societal, but also technical, landscape aesthetic and cultural issues have to be addressed.

4. WATER POLLUTION

Along with the emerging problem of water scarcity, one of the most significant water problems of modern times, in some regions of the world even reaching crisis levels, is water pollution. Since ancient times people have always built their settlements near rivers, or water bodies, primarily to secure sufficient water supplies. Rapid and extensive growth of urbanization, growth of population and growth and development of industrial activities over time generated large amounts of waste, especially in urban areas, and most of this waste ended up in the nearby water bodies. With time these waters became so degraded in their quality that they could not be used for the previous purpose (use in households or in industry) and required special attention due to their ecological status. With the development of global environmental awareness and knowledge about pollution causes, but also pollution consequences, people started paying more attention to pollution issues and environmental awareness was even further risen with the development of environmental protection legislation.

There is no clean water, that is pure H_2O, in nature. Due to the unique water properties, which make it an universal solvent, water in nature always contains some quantities of dissolved gasses, minerals and microorganisms. Water that contains low levels of suspended or dissolved solids, low levels of dissolved adverse gasses, as well as low biological content is considered to be clean, or water of high quality.

4.1. WATER QUALITY AND INDICATORS OF WATER QUALITY

The necessary quality of water varies by its' use. Quality water targets (QWTs) are usually set for drinking water, water for domestic/ industrial use or as remediation targets of polluted water ecosystem. For instance, high quality water is required only for drinking, but water of such quality is not necessary for some industrial processes or agriculture. QWTs for drinking water are set by national standards according to international standards. Different industry standards set QWTs for water use in specific industrial processes.

The guidelines for setting standards of drinking water quality are prepared by the World Health Organization (WHO) and according to those guidelines and recommendations, water and health regulators and policymakers create national standards. In 1983-1984 WHO published the first *Guidelines for Drinking-water Quality* in three volumes, which followed previous WHO International Standards. The standards set generally acceptable levels or maximum allowable concentrations (MACs) of various substances contained in water. When the levels of dissolved substances and microorganisms are below MACs, water is considered to be of sufficient quality for a certain use. Example of the WHO guideline values for naturally occurring chemicals and for chemicals from agricultural activities in drinking water are shown in Table 1 and Table 2. In Table 3 some MACs from the European Union Drinking Water Directive are shown.

Table 1 The WHO guideline values for naturally occurring chemicals that are of health significance in drinking water (WHO, 2006)

Chemical	Guideline value, mg/l	Remarks
Arsenic	0.01 (P)	
Barium	0.7	
Boron	0.5 (T)	
Chromium	0.05 (P)	For total Chromium
Fluoride	1.5	Volume of water consumed and intake from other sources should be considered when setting national standards
Manganese	0.4 (C)	
Molybdenum	0.07	
Selenium	0.01	
Uranium	0.015 (P,T)	Only chemical aspects of uranium addressed

Legend: **P**-provisional guideline value, as there is evidence of a hazard, but the available information on health effects is limited; **T**-provisional guideline value because calculated guideline value is below the level that can be achieved through practical treatment methods, source protection, etc.; **C**- concentrations of the substance at or below the health-based guideline value may affect the appearance, tase or odour of the water, resulting in consumer complains.

Table 2 The WHO guideline values for chemicals from agricultural activities that are to health significance in drinking water (WHO, 2006)

Non-pesticide	**Guideline value mg/l**	**Remark**
Nitrate (as NO_3^-)	50	Short-term exposure
Nitrite (as NO_2^-)	3 0.2 (P)	Short-term exposure Long-term exposure
Pesticides used in agriculture	**µg/l**	
Alachlor	20[b]	
Aldicarb	10	Applies to aldicarb sulfoxide and aldicarb sulfone
Aldrin and dieldrin	0.03	For combined aldrin plus dieldrin
Atrazine	2	
Carbofuran	7	
Chlordane	0.2	
Chlorotoluron	30	
Cyanazine	0.6	
2,4-D (2,4-dichlorophenoxyacetic acid)	30	Applies to free acid
2,4-DB	90	
1,2-Dibromo-3-chloropropane	1[b]	
1,2-Dibromoethane	0,4[b] (P)	
1,2-Dichloropropane (1,2-DCP)	40 (P)	
1,3-Dichloropropane	20[b]	
Dichloroprop	100	
Dimethoate	6	
Endrin	0.6	
Fenoprop	9	
Isoproturon	9	
Lindane	2	
MCPA	2	
Mecoprop	10	
Methoxychlor	20	
Metolachlor	10	
Molinate	6	
Pendimethalin	20	
Simazine	2	
2,4,5-T	9	
Terbuthylazine	7	
Trifluralin	20	

Legend: P- provisional guideline value, as there is evidence of a hazard, but the available information on health effects is limited. **[b]** For substances that are considered to be carcinogenic, the guideline value is the concentration in drinking water associated with an upper-bound excess lifetime cancer risk of 10^{-5} (one additional cancer per 100 000 of the population ingesting drinking water containing the substance at the guideline value for 70 years). Concentrations associated with estimated upper-bound excess lifetime cancer risks of 10^{-4} and 10^{-6} can be calculated by multiplying and dividing, respectively the guideline value by 10.

Table 3 Some MACs from The European Union Drinking Water Directive- Directive (EU) 2020/2184 (Directive (EU) 2020/2184)

Substance	MAC
Acrylamide	0.10 µg/l
Antimony	10.0 µg/l
Arsenic	10 µg/l
Benzene	1.0 µg/l
Benzo(a)pyrene	0.01 µg/l
Boron	1.5 mg/l
Bromate	10 µg/l
Cadmium	5.0 µg/l
Chromium	50µg/l
Copper	2.0 mg/l
Cyanide	50 µg/l
1,2-dichloroethane	3.0 µg/l
Epichlorohydrin	0.10 µg/l
Fluoride	1.5 mg/l
Lead	10 µg/l
Mercury	1.0 µg/l
Nickel	20 µg/l
Nitrate	50 mg/l
Nitrite	0.50 mg/l
Pesticides	0.10 µg/l
Pesticides - Total	0.50 µg/l
Polycyclic aromatic hydrocarbons (PAH)	0.10 µg/l
Selenium	20 µg/l
Tetrachloroethene and Trichloroethene	10 µg/l
Trihalomethanes — Total	100 µg/l
Uranium	30 µg/l
Vinyl chloride	0.50 µg/l

Quality of water depends on its composition, properties, and concentrations of certain substances. Quality of water is evaluated by the following groups of indicators (Tedeschi, 1997; Mayer, 1993):

1. **Physical indicators**- They determine water appearance, colour, odour, taste, and temperature. Physical indicators of water quality are:
    a. ***Dispersed substances***- Dispersed or suspended substances can be organic (live organic matter-microorganisms, products of metabolism and dead organic matter-particles of dead organisms) or inorganic (sand, clay, silt). Dispersed or suspended substances are typical for surface waters.

    b. ***Turbidity***- Turbidity is a consequence of dispersed matter, particularly colloids, microorganisms, and gas bubbles. It impacts the ability of sunlight penetration into a body of water and thus photosynthesis.

    c. ***Colour***- Colour of water, as a result of dissolved substances, is known as "*true colour*", and the one resulting from substances dispersion is called "*apparent colour*".

    d. ***Taste and odour***- Water odour and taste usually come along, that is, waters that expose odour also have taste. The opposite is not the case. Namely, saline water has taste but has no odour. Taste and odour of water are the consequence of organic matter decay, live organisms' metabolism (particularly algae), dissolved solid (salts) and gaseous substances (for instance hydrogen sulphide).

    e. ***Temperature***- Water temperature is related to the environmental temperature and changes throughout the year. Temperature has impact on water physical and chemical properties. Changes in water temperatures are usually caused by release of industrial cooling waters.

2. **Chemical indicators**- Chemical substances in water can be divided into three categories:
    - substances normally occurring in waters;
    - substances which, by their composition or concentration do not affect use of water, unless present in large quantities;
    - substances which, by their composition or concentration, make water unusable for certain purposes. These substances can be poisonous.

    Due to the sated, chemical indicators of water are:
    a. ***Total dissolved substances***- Ions usually present in waters are shown in Table 4.

Table 4 Naturally occurring ions in waters (Tedeschi, 1997)

Main substances 1.0-1000 mg/l	**Other substances 0.01-10.0 mg/l**
Sodium	Iron
Calcium	Strontium
Magnesium	Potassium
Bicarbonates	Carbonates
Sulphates	Fluorides
Chlorides	Nitrates
	Boron
	Silicon

b. ***Concentration of hydrogen ions (pH)***- Concentration of hydrogen ions is a reference of the acidity or alkalinity of water. pH is defined as negative logarithm of the concentration of hydrogen ions. Natural, unpolluted waters have pH values between 5.5 and 8.6. pH values for drinking water range between 6.5 to 8.5 (Omer, 2019). The acidity of unpolluted water depends upon chemical balance of dissolved carbon dioxide (CO_2), carbonate ions (CO_3^{2-}) and bicarbonate ions (HCO_3^-).

c. ***Alkalinity***- Beside CO_3^{2-} and HCO_3^-, water alkalinity is dictated by hydroxide ions (OH^-), silicates ($HSiO_3^-$), borates ($H_2BO_3^-$), phosphates (HPO_4^{2-}, $H_2PO_4^-$) and hydrogen sulphates (HS^-).

d. ***Water hardness*** (degree of mineralisation of water)- Water hardness is determined by concentration of polyvalent metal cations (primarily calcium and magnesium cations). Water hardness can be carbonate (so-called "*temporary hardness*"; consequence of the presence of carbonate ions) or non-carbonate (so-called "*permanent hardness*"; caused by sulphates and chlorides). Generally, groundwater is harder than surface water. Classification of water according to its hardness is shown in Table 5.

Table 5 Classification of water according to its hardness (Omer, 2019)

Water classification	**Total hardness mg/L as $CaCO_3$**
Soft	< 50
Moderately hard	50-150
Hard	150-300
Very hard	> 300

e. ***Dissolved gasses***- Gas solubility in water is shown in Table 6. One of the most important parameters of water quality is the concentration of dissolved oxygen. The more oxygen dissolved in water, the better the quality of water. Except on temperature (as it could be seen from the Table 6), the dissolution of oxygen in water also depends on pressure and water salinity (the concentration of dissolved salts in water).

Table 6 Gas solubility in water (Tedeschi, 1997)

T (˚C)	Gas (1L gas/1L water @ 1 bar)									
	Air	O_2	N_2	H_2	CO_2	H_2S	Cl_2	NH_3	SO_2	O_3
0	0.0373	0.0489	0.0235	0.0215	1.713	4.621	4.61	1.135	75.00	0.640
5	0.0330	0.0429	0.0208	0.0204	1.424	3.935	3.75	1.005	62.97	0.571
10	0.0293	0.038	0.0186	0.0196	1.194	3.362	3.095	881	52.52	0.502
15	0.0265	0.0342	0.0168	0.0188	1.019	2.913	2.635	778	43.45	0.432
20	0.0242	0.0310	0.0154	0.0182	0.878	2.554	2.260	681	36.31	0.331
25	0.0233	0.0283	0.0143	0.0175	0.759	2.257	1.985	595	50.50	0.273
30	0.0208	0.0261	0.0125	0.0170	0.665	2.014	1.769	521	25.87	0.207
35	0.0195	0.0244	0.0118	0.0167	0.592	1.811	1.570	460	22.00	0.151
40	0.0184	0.0231	0.0109	0.0164	0.533	1.642	1.414	395	18.91	0.103
50	0.0168	0.0209	0.0102	0.0161	0.437	1.376	1.204	294	15.02	0.045
60	0.0157	0.0195	0.0097	0.0160	0.365	1.176	1.006	198	11.09	
70	0.0150	0.0183	0.0096	0.0160	0.319	1.010	0.848		8.91	
80	0.0146	0.0176	0.0095	0.0160	0.275	0.906	0.672		7.27	
90	0.0144	0.0172	0.0095	0.0160	0.246	0.835	0.380		6.16	
100	0.0144	0.0170		0.0160	0.220	0.800				
110		0.0168			0.204					
120		0.0169			0.194					
130		0.0170								
140		0.0172								

f. ***Organic matter***- In natural waters organic matter can be present as dispersed or dissolved. The origin of organic matter in water are biochemical processes in water, soil leaching by rain or urban and industrial wastewaters. The most significant groups of organic matter in wastewaters are proteins (40-60%), carbohydrates (25-50%) and lipids (around 10%). Total organic matter in water can be divided into biologically degradable and biologically non-degradable organic matter. Microorganisms in water use biologically degradable organic matter as source of food. During the process of biodegradation of organic matter oxygen is used. In aquatic environment with enough oxygen dissolved, aerobic processes take place, and in environment of insufficient quantities of oxygen, anaerobic processes occur. Indicator of biodegradable organic matter is called biochemical oxygen demand (BOD). Normally, wastewater has high organic content. The organic content in water is measured by biochemical oxygen demand (BOD) and chemical oxygen demand (COD). While BOD is used for measuring biodegradable organic matter, COD is used for measuring all organics (the biodegradable and non-biodegradable). The course of carbon and nitrogen substances' degradation by biochemical oxygen demand is shown in Figure 13. Non-biodegradable organic matter that naturally occurs in waters are tannins, lignin substances, cellulose, while pesticides and detergents have anthropogenic sources. Out of pesticides the most harmful are the organochlorine pesticides (aldrin, dieldrin, DDT, endrin, lindane), polychlorinated biphenyls (PCBs) and organophosphorus pesticides (diazinon). PCBs can also be found in some industrial wastewaters that contain plastics, dyes and varnishes or electrical insulation material).

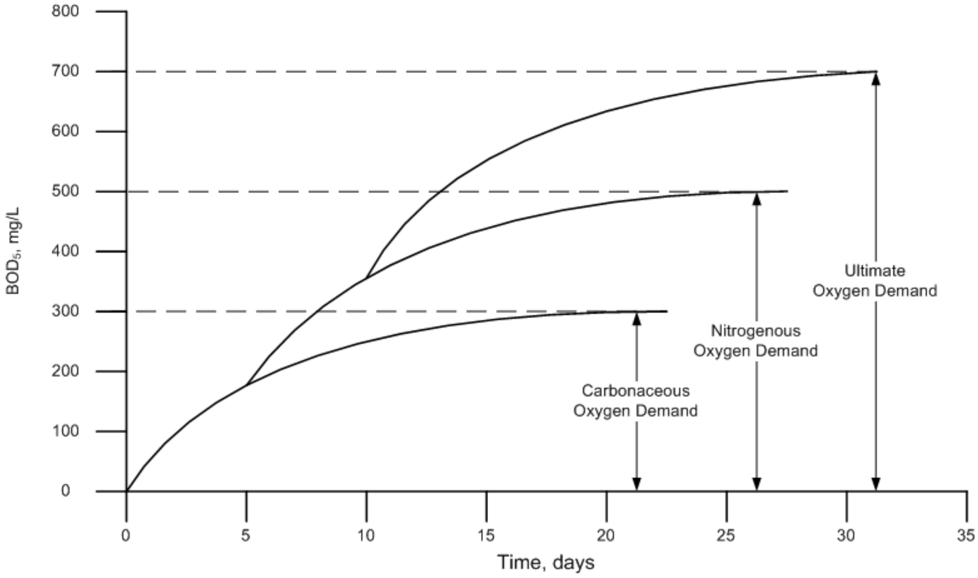


Figure 13 The course of carbon and nitrogen substances' degradation by biochemical oxygen demand (Eckenfelder, 2000)

g. ***Nutrients***- Nutrients in water are all the substances necessary for the production of primary organic matter (algae, green plants). These are primarily nitrogen, phosphorus, calcium, sulphur, and magnesium (macronutrients) and iron, manganese, copper, zinc, boron, silicon, molybdenum, chlorine, vanadium, and cobalt. In water environment with enough oxygen nitrification process takes place. Nitrification is the process of organic matter biodegradation in which nitrogen compounds (primarily ammonia) is oxidized to nitrite and nitrate. It is done by nitrification bacteria. After almost all oxygen is consumed in the nitrification process, the denitrification bacteria (heterotrophs, anaerobes) start the denitrification process- the reduction of nitrite and nitrate to nitrogen or ammonia. Nitrification and denitrification are essential parts of nitrogen cycle.

h. ***Metals***- Metals are present in water as a result of soil leaching and minerals dissolving. Increased concentrations of metals in water have anthropogenic sources (industry wastewater, household wastewater and agriculture wastewater).
i. ***Other chemical indicators*** (fluorides, chlorides, sulphates, cyanides).

3. **Biological indicators**- Biological indicators are used for identification of the changes in ecosystem caused by changes of abiotic factors. They show the health of flora and fauna in aquatic ecosystem. Undisturbed ecosystem is combined of various species of organisms coming in moderate number of individual organisms. Disturbed ecosystem is characterised by limited number of species, but with numerous numbers of organisms of a specific species. Widely used biological indicators of water quality are:
   a. ***Degrees of saprobity***- There are four degrees of saprobity by which waters are classified as (Tedeschi, 1997):
      - *I. class waters*- waters that contain high concentration of dissolved oxygen, low turbidity, and total number of bacteria lower than $100/1cm^3$. The so-called oligosaprobic organisms as biological indicators of water quality in I. class waters are sensitive to pH value changes, dissolved oxygen concentrations and organic matter content. I. class water is water in mountain springs and mountain lakes.
      - *II. class waters*- waters that contain enough dissolved oxygen (but less than I. class waters), turbidity is low and total number of bacteria is lower than $100\,000/1cm^3$. The so-called beta-mezosaprobic organisms living in those waters are sensitive to changes of pH value, changes of dissolved oxygen concentrations and high concentrations of rotting products. II. class water is water in big lakes and lower parts of big unpolluted rivers.
      - *III. class waters*- waters contaminated by organic matter. Due to high content of organic matter, which they use as source of food, beside bacteria, which number in those waters exceeds $100\,000/1cm^3$, those waters contain high number of algae (cyanobacteria and green algae) and protozoa. The so-called alpha-mezosaprobic organisms living in those water are adapted to changes of pH values and oxygen concentrations, and to high values of ammonia, but are sensitive to hydrogen sulphide (H_2S). III. class of waters are bayous with slow water exchange, contaminated rivers, marshes, and irrigation canals.
      - *IV. class waters*- polluted waters characterised by anaerobic conditions, high content of bacteria ($>150\,000/1cm^3$), high turbidity, colour, and odour (due to H_2S production).

   b. ***Degree of biological production***- The degree of biological production in water depends upon the content of nutrients. Natural eutrophication (introduction of nutrients to the water system), as a consequence of matters' cycles in nature, is a slow process. On the other hand, anthropogenic introduction of nutrients into natural water systems, can quickly result with excess of algae, particularly blue-green algae (cyanobacteria), and bacteria, which by its activities will further contribute to degradation of water quality.

c. ***Microorganisms***- Water is favourable environment for the development of microorganisms. Beside microorganisms that commonly exist in water, like decomposers and producers of organic matter, with wastewaters or soil leaching, many other microorganisms find their way to water bodies. The most common microorganisms found in waters are bacteria, eumycota, rickettsiae, viruses and protozoa. Some of the microorganisms coming to water bodies are pathogenic, primarily the ones coming from human or animal faeces. Group of bacteria called faecal coliforms are often used as indicators of water pollution with faecal waste. The most know bacteria coming from that group of bacteria are *Escherichia coli* and *Enterococci*.

d. ***Toxicity***- Toxicity is a measure of adverse effect of a matter on living organisms. Toxic matter is every matter that causes disease of living organisms, abnormal behaviour, cancerogenic and genetic changes, physiological disorders, physical deformation and death. Toxicity of substances is determined by biotests that include using specific species and exposing it to concentration, or set of concentrations, of certain matter during certain time period (4 hours, 24 hours, 48 hours, 72 hours, 96 hours). The concentration that causes death of 50% of the exposed population is called lethal concentration (LC_{50}) (Tedeschi, 1997).

e. ***Difference index***- Difference index is mathematical expression for biological community structure. It is calculated by (Tedeschi, 1997):

$$H' = \sum_{i=1}^{S} \frac{N_i}{N} log_2 \frac{N_i}{N} \quad (2.1)$$

Where:
N_i- number of organisms of *i* species,
N- total number of organisms,
s- total number of species.

Rough estimation of water pollution by difference index is as follows (Tedeschi, 1997):
Major pollution H'<1.0
Moderate pollution H'= 1.0-3.0
Clean water H'>3.0

4. **Radiological indicators**- The origin of radioactive matters in water can be natural (naturally occurring radioactive matter, NORM) or anthropogenic (nuclear energy plants, mining sites, nuclear waste disposal sites etc.).

4.2. TYPES OF WATER POLLUTION

Regarding the degradation of water quality, water systems can be contaminated or polluted. Both terms refer to changes in water quality or composition by harmful substances or energy introduced directly or indirectly, either naturally or by human activities, to water system. The difference is in the extend and severity of the consequences. Namely, in case of water contamination, presence of substances or energy in concentrations or quantities above background, results in water less suitable for drinking or domestic, agricultural, industry, recreational, wildlife or other use. In case of water pollution water becomes threat to living organisms and it cannot be used anymore. Basically, water pollution is contamination that results with more adverse consequences. According to the World Health Organisation (WHO), the polluted water is one whose composition has been changed to the extent that is unusable.

Exposure to polluted water (by drinking, bathing, swimming, consuming food that was in contact with polluted water, or even breathing vapors of polluted water) can cause a variety of diseases ranging from simple intoxication to deadly results. As stated before, water pollution is a phenomenon that inevitably follows industrialization and urbanization, and it is one of the pressing problems of the world today. As shown in Figure 14, there is almost a quarter of worlds' population without access to safe drinking water. According to the Natural Resources Defense Council, polluted water globally kills more people each year than war and all other forms of violence combined (www.nrdc.org).

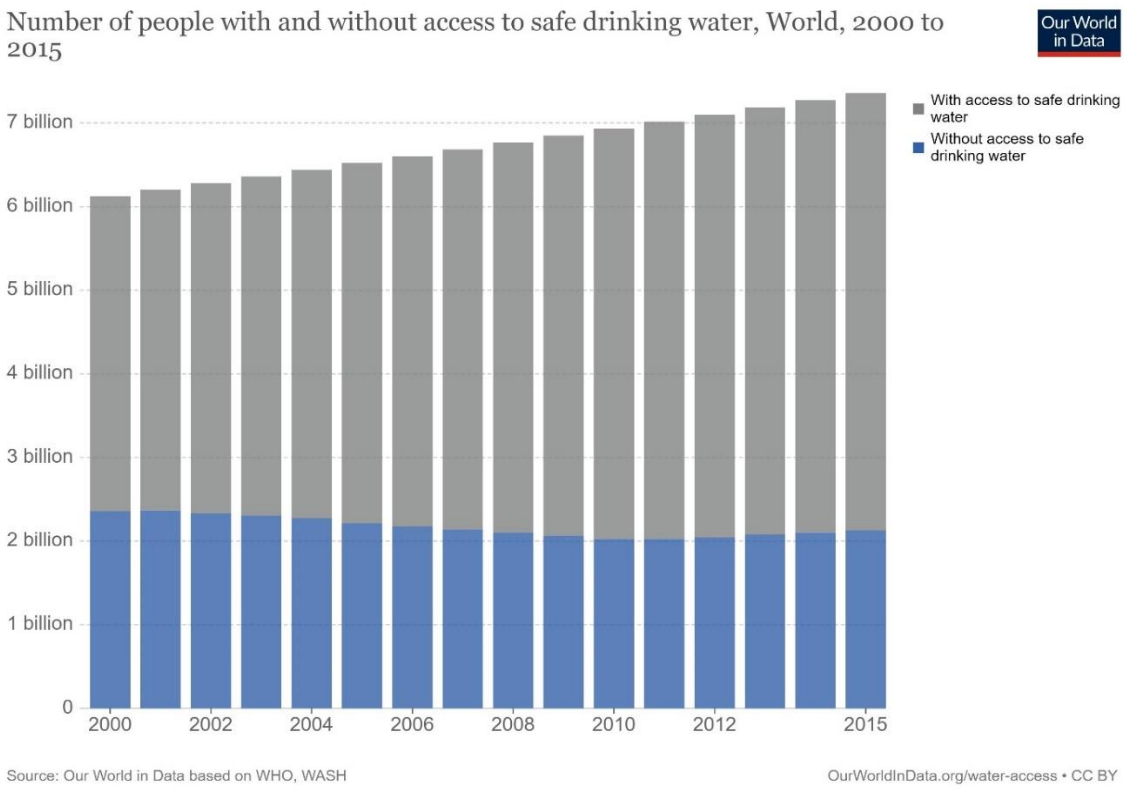


Figure 14 Number of people with and without access to safe drinking water in period 2000-2015 (https://ourworldindata.org)

Polluted water exhibits certain odour, turbidity, lack of water transparency, high concentrations of chemical oxygen demand (COD), biological oxygen demand (BOD) and organic and inorganic contaminants. Depending on causes of water quality change, that is which, previously mentioned quality indicators have been mostly affected, water pollution can be (Mayer, 2004):

1.) Physical
2.) Chemical
    a. Inorganic
    b. Organic
3.) Biological
4.) Radiological

Substances (polluters) causing water pollution can be generally divided as pathogens (bacteria, viruses, or protozoa) causing primarily biological water pollution, inorganic material causing physical, chemical or radiological pollution, organic material causing chemical pollution and macroscopic pollutants, causing physical pollution (https://sciencing.com). Macroscopic pollutants are visible pollutants in water bodies like plastics.

4.3. TYPES OF SOURCES OF WATER POLLUTION

Sources of water pollution differ by their activity and their form (Mayer, 1993). By their form, sources of water pollution can be classified as (Mayer, 1993; www.environmentalpollutioncentres.org):

1. **Point sources**
   Point sources of water pollution have localised source, a point at which pollution is generated and as such it can be detected and controlled. From a point source, pollutants spread out in a plume having highest concentrations of pollutants near the source. Typical point sources of water pollution are industrial or agricultural wastewater discharges, landfills, or wastewater treatment plants (Figure 15). By the development of legislation, regulation, and consequently wastewater treatment and monitoring, water pollution from point sources has been largely reduced, especially in the developed countries.

Figure 15 Typical point source of water pollution (http://www.waterencyclopedia.com)

2. **Non-point (dispersed) sources**

   Non-point, dispersed, sources do not have a specific point of origin. These are the unidentified sources. Non-point water pollution occurs when water runoff from storms (Figure 16), snow melting or irrigation comes in contact with polluters like fertilizers, pesticides, paint, petroleum products, garbage (animal waste, plastics…) etc. and caries it to water bodies.

Figure 16 Rain runoff is a typical non-point source of water pollution (http://www.waterencyclopedia.com)

By the activity, water pollution sources can be seen as (Mayer, 1993):

1. **Active sources**

   Active water pollution sources are the ones that have been identified as water polluting sources. These are the sources for which is known that they emit some harmful substances or energy into water bodies. Furthermore, active water pollution sources can be permanent (constantly emitting harmful substances or energy into water bodies; for example, industrial discharge), or intermittent (periodically emitting harmful substances or energy into water bodies; for example, agricultural fields in time of fertilization).
2. **Potential sources**

   As the name indicates, these sources do not emit harmful substances into water bodies in normal conditions but could cause water pollution in case of exceptional circumstances like accidents or failures (for instance oil/gas pipelines, sewage pipelines etc.).

4.4. LARGE SOURCES OF WATER POLLUTION

4.4.1. AGRICULTURE

One of the biggest polluters of water bodies, both groundwater and surface water, is agriculture. Water polluting substances in agriculture come from livestock farming, and production, process, transport and storing of food crops, non-food crops (e.g., biofuel crops) and animal feed. As regarding agricultural pollution of water bodies, the most significant pollutants are nitrogen and phosphorous fertilizers, chemical pesticides (herbicides, insecticides, fungicides etc.) from crop production and animal waste and wastewater from livestock farms.

Nutrient pollution caused by excess of nitrogen and phosphorus in water (runoff from agricultural fields and manure lagoons) contributes to eutrophication, one of the biggest problems of water pollution today. The eutrophying emissions per kilogram of food production are shown in Figure 17. Namely excess of nitrogen and phosphorus cause blue green algae blooms, which lead to hypoxia (which is used for algae decomposing process) and finally to creation of so-called "dead zones" (Figure 18).

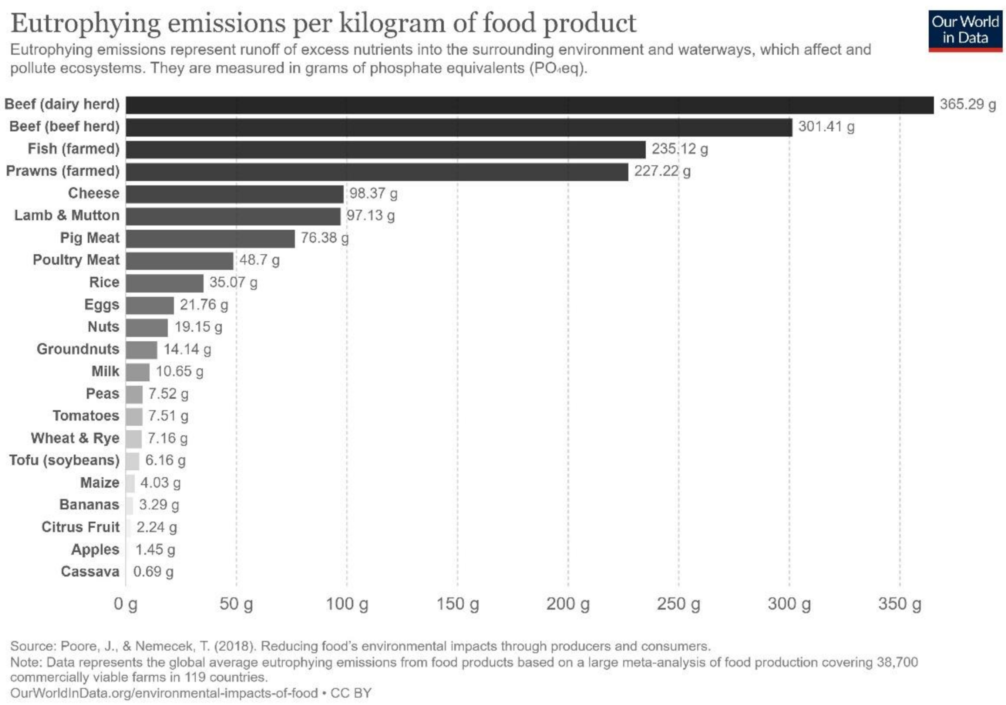


Figure 17 Eutrophying emissions per kilogram of food production (https://ourworldindata.org)

Figure 18 Toxic green algae bloom (www.nrdc.org)

The problem with animal waste and water pollution nowadays are not only pathogens related to runoff from agricultural fields, where animal manure is usually applied, or leaks, spills, or runoff from manure lagoons, but also to use of antibiotics in livestock production. Namely, there is widespread use of antibiotics in meat production (not to treat sick animals). In the United States of America (USA) $^{2}/_{3}$ of antibiotics used as human medicine are used in livestock farming (www.nrdc.org). This widespread use of antibiotics leads to proliferation of antibiotic- resistant bacteria.

4.4.2. SEWAGE

Sewage is the term used for wastewater form households, services, industry, agriculture and runoff from roads and other impermeable surfaces. According to the UN more than 80% of the worlds' wastewater is released into the environment without any treatment (in some underdeveloped countries even 95%) (www.nrdc.org). Domestic sewage is significant source of pathogens (bacteria and viruses), organic substances and nitrates and phosphates (that cause eutrophication). Industrial sewage, depending on type of industry and technological processes involved, can contain heavy metals, acids, bases, salts, biocides, hydrocarbons, phenols and polycyclic aromatic compounds, radioactive matters etc.

4.4.3. OIL SPILLS

Most of oil that comes to water bodies comes as runoff from roads, parking lots and other solid surfaces. Significant amount of oil also comes from oil spills. In Figure 19 the sources of marine oil pollution can be seen. It is estimated that around 1 million tons of oil ends up each year in seas and oceans (www.nrdc.org). Most of that oil, as it can be seen from Figure 19, comes from land.

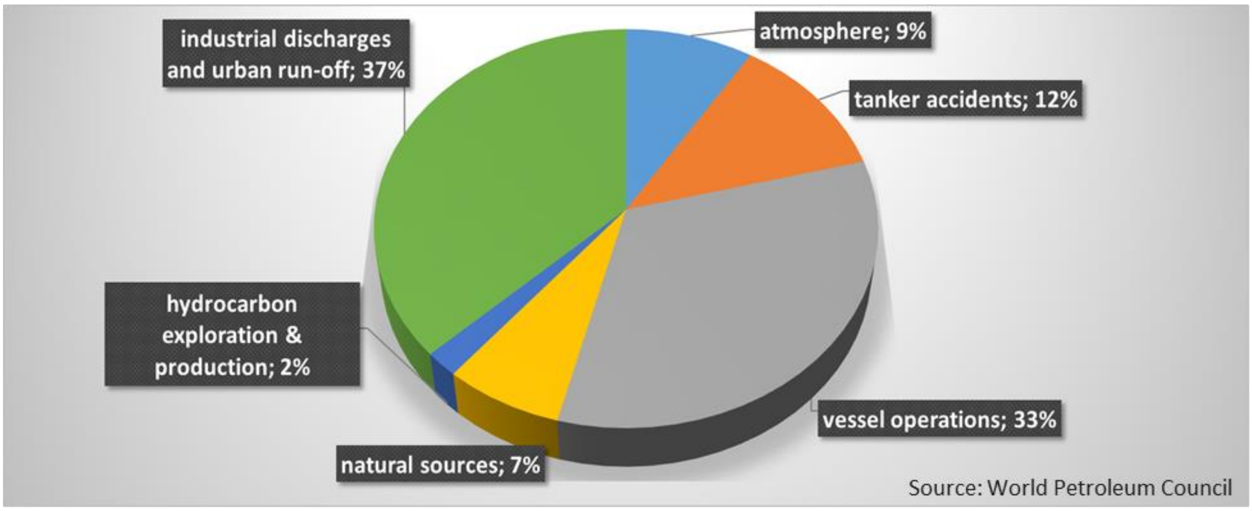


Figure 19 Sources of marine oil pollution (www.world-petroleum.org)

4.4.4. LITTER

Litter comes in variety of sizes, materials, and shapes. Illegal dumping of litter, which can be caried to the surface water bodies by wind or rain runoffs or leached to groundwater, but also runoffs from landfills, significantly contributes to water pollution. In last several decades special attention regarding water pollution is put on plastics which has become significant contributor to water pollution. Namely, excessive use of plastics, especially single-use plastics like plastic bottles, plastic bags, coffee lids, plastic cutlery etc., has led to creation of excessive amounts of plastic waste which takes hundreds of years to degrade, but only to become microplastic which can even easily enter water systems. It is estimated that around 8 million tones of plastic leaks into oceans and waterways every year (https://doulton.com). According to estimations, there are around 270 million tons of plastic waste in worlds' oceans (Figure 20).

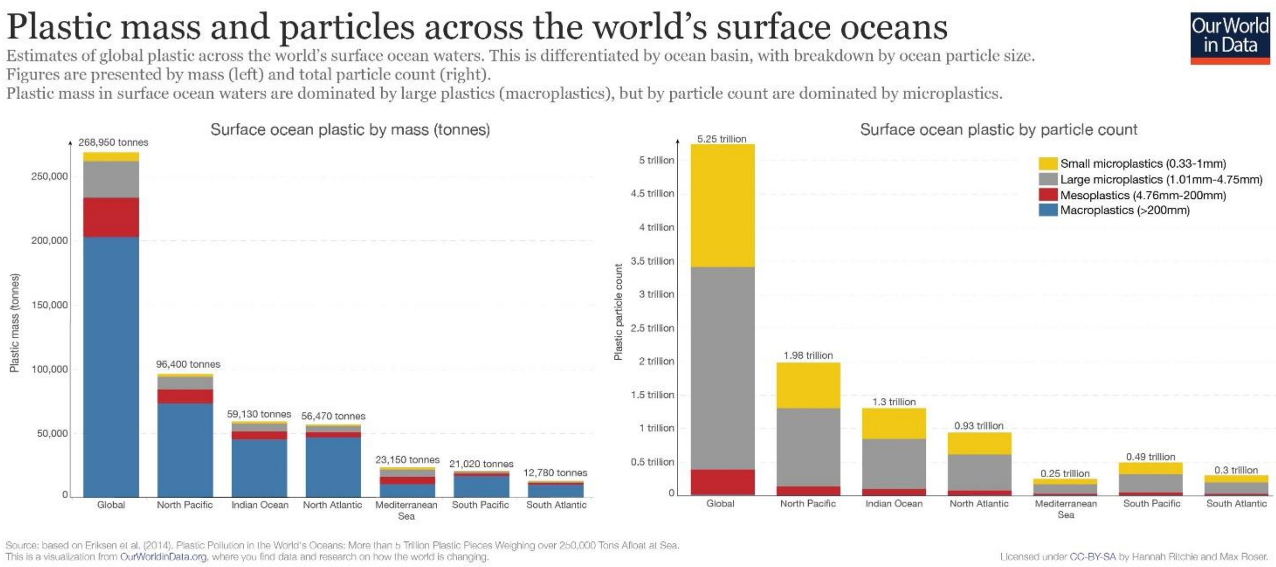


Figure 20 Plastics in worlds' oceans (https://ourworldindata.org)

5. CONCLUSION

Water is the most widespread liquid on Earth and it is the basis of life on Earth. Most of the water on Earth is saline water not suitable for direct consumption. Only less than 3.0% is fresh water, and out of that, almost 70.0% is in solid state (glaciers and ice caps). Due to its unique properties water acts as universal solvent, which makes it prone to pollution/ contamination. Polluted water contains substances which degrade its quality and make it unsuitable for certain use. Water pollution can be classified as physical (degradation of physical indicators of water quality like appearance, colour, taste and temperature), chemical (degradation of chemical indicators of water quality- presence of organic and inorganic substances), biological (degradation of biological indicators of water quality like saprobity, degree of biological production, toxicity, presents of microorganisms, difference index) and radiological (degradation of radiological indicators of water quality- presence of radiological substances).

Water gets polluted either by natural (natural disasters) or, mostly, anthropogenic activities. The sources of water pollution are classified as point and non-point (dispersed) sources. By their activity the water pollution sources can be active or potential. One of the biggest polluters of water bodies, both groundwater and surface water, is agriculture. Beside mentioned, large sources of water pollution are also sewage, oil spills and litter (especially plastics).

In last few decades with the accelerated problems and consequences of climate change, beside water pollution, also water scarcity take up special attention and has become one to the major challenges in the 21st century.

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