ESCOLA SUPERIOR DA CETESB
GESTÃO DO CONHECIMENTO AMBIENTAL

2017

MÓDULO 2 - WATER QUALITY VARIABLES AND THE OBJETIVES OF WATER QUALITY DIAGNOSIS

CLASSES SUPPORTING MATERIAL:

- SAMPLING AND PRESERVATION OF WATER AND SEDIMENT SAMPLES
- WATER QUALITY MONITORING AND ASSESSMENT

Cursos e Treinamentos

Gestão do Conhecimento

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CETESB • ENVIRONMENTAL COMPANY OF SÃO PAULO STATE

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To promote and monitor the execution of environmental and sustainable development public policies, ensuring the continuous improvement of environmental quality in order to address the expectations of the State of São Paulo's society.

VISION

To improve the standards of excellence in environmental management and the services provided to users and to the population as a whole, ensuring CETESB's ongoing evolution in acting as a national and international reference in the environmental field and in protecting public health.

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The values, principles and standards that guide CETESB's actions are established in its Code of Ethics and Professional Conduct.

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São Paulo, Abril de 2017

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UNESCO – United Nations Educational, Scientific and Cultural Organization

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FOREWORD

Water is one of the most important assets for biological activity and throughout the universe it has been sought out as something essential for life, yet it is unfortunately treated in an inconsequential way by most members of humanity. The human perception is that water is infinite and inexhaustible. Because of this, it is inadequately approached in ecological terms.

A full understanding of the correlation water-quality and quantity versus multiple uses - must be fully understood in order to change this behavior so as to leave future generations with possibilities for survival that unite their basic needs with environmental preservation.

The conception of a course of this magnitude indicates that there is a need for a continuous knowledge acquisition that requires topics that might gradually lead us to a comprehensive understanding of the natural aquatic environment (increasingly rare) and its progressive alterations, regarding external as well as internal metabolism in the aquatic ecosystem, in order to fully understand nature and the influence of human beings.

Based on these initial conceptualizations, the course will therefore be aimed at learning about the various types of aquatic environments and their main compartments, emphasizing intrinsic inorganic and organic characteristics, correlations between changes that are native and non-native in origin and those that are primarily considered to be natural environments without any anthropogenic interference.

Thus, over time, the knowledge acquired in each of these modules will lead to an increasingly richer understanding of the influence that human actions have on the balance of aquatic ecosystems.

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Carmen Lucia V. Midaglia holds a degree in Geography from the Faculty of Philosophy, Literature and Human Sciences at USP - Geography Dept. (1984), and a degree as a Translator and Interpreter in English from the the Ibero-American Faculty of Literature and Human Sciences (1982). She did her postgraduate studies in "Rural and Land Ecology Survey" at the ITC-Faculty of Geo-Information Science and Earth Observation (ITC) at the University of Twente in Enschede, The Netherlands. She received a master's degree in Human Geography from the Faculty of Philosophy, Literature and Human Sciences at USP - Geography Dept. (1994). She has experience in the environmental area with an emphasis on the monitoring of water quality. She completed her PhD in 2009 at FFLCH-Geography, presenting the proposal for the Index of a Spatial Scope for the Monitoring of Surface Water (IAEM), focusing on the spatial management of water resources and its relationship to population growth, demonstrating the vulnerabilities caused by anthropogenic pressure.

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A Biologist at CETESB since 1980, Claudio Roberto Palombo graduated from the Institute of Biosciences at the University of São Paulo and has a bachelor’s degree in Ecology (1978). He also received a master's degree (1989) and doctorate (1997) from the Department of General Ecology in the Institute of Biosciences at the University of São Paulo. He has experience in limnology with an emphasis on altered environments. He is a University Professor and Technical Analyst of FEHIDRO Projects related to aquatic ecosystems and has developed methodologies for integrated weed management.

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A Sanitary Engineer trained at the Mauá Institute of Technology (2001) and has a master’s degree in Civil Engineering from the Polytechnic School of the University of São Paulo (2005), Gabriela de Sá Leitão de Mello was an environmental analyst at the Environmental Company of São Paulo State - CETESB from August 2007 to September 2012 working in the fields of water quality and licensing and inspection. From 2002 to 2015, she was a professor at the University Center of the Mauá Institute of Technology and a professor at the Faculty of Engineering of the University Center of the Santo André Foundation from 2005 to 2015. She taught undergraduate courses including Introduction to Environmental Engineering, Environmental Pollution and Sanitation, as well as postgraduate courses. She began her doctorate in 2012 at USP's School of Public Health completing all her credits, but stopped her enrollment in 2014 due to a change of country. In 2015, she lectured at two universities in Peru: Pontificia Universidad del Peru - PUCP and Universidad Científica del Sur. She is currently working with Golder Associates as a Specialist in Water Quality.

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SUMMARY

WATER QUALITY VARIABLES AND THE OBJECTIVES OF WATER QUALITY DIAGNOSIS

ENG. SAN. GABRIELA MELLO

Cadernos da
Gestão do Conhecimento

WATER QUALITY VARIABLES AND THE OBJECTIVES OF WATER QUALITY DIAGNOSIS

Introduction

Water quality in water bodies is a result of the natural conditions and anthropogenic activities taking place in the area. Thus, the water quality of a hydrographic basin will be determined by its preservation level, the use and occupation of the area's soil, the soil's characteristics and the types of vegetation cover that are present.

Even in a preserved hydrographic basin, for example, there is natural amount of suspended solids into the body of water, which can increase water turbidity levels. Anthropogenic activities, in turn, may cause more intense alterations in water quality, both in an occasional way, as in the release of domestic sewage and industrial effluents into the water, and also in a diffuse way, through the application of agrochemicals and fertilizers, which, during moments of rainfall, drain into the water bodies on the surface

Chapters 1 and 2 of this course module will discuss in detail some of the key water quality variables, also called quality indicators or parameters. It should be emphasized that there are hundreds of water quality variables and that the choosing of which variables should be used to assess the quality of a particular body of water will depend on the objective. One example might be checking the compatibility of the water quality with its intended use and with the available resources. In a monitoring program for the periodic monitoring of water quality, the selection of variables should take into account the applicable legislation and the parameters that are relevant to the region. In order to facilitate communication with the public, environmental control agencies can convert the results of their analyses into water quality indexes. As an example, in Brazil, the Environmental Company of the State of São Paulo - CETESB applies the following indexes to the results obtained in the monitoring program:

- WQI – Water Quality Index
- RWQUIPWS – Raw Water Quality Index for Public Water Supply
- TSI – Trophic State Index
- WQIPAL – Water Quality Index for the Protection of Aquatic Life and Aquatic Communities

In this module, the following physical variables will be studied: Turbidity, True Color, Series of Solids, Conductivity, Temperature and Transparency; (nitrogen forms and phosphorus forms), pH, Metals (aluminum, manganese, iron, arsenic, barium, cadmium, chromium, copper, cobalt, lead, mercury, silver, nickel, selenium and zinc), chloride, total alkalinity, sulphate, hardness, fluoride, oils and greases, phenolic compounds, detergents, organochlorine pesticides, polycyclic aromatic hydrocarbons - PAHs, trihalomethane formation potential, polychlorinated biphenyls- PCBs and Emerging Pollutants.

Changes in water quality, as evidenced by changes in levels of quality parameters, may restrict their intended uses, causing damage to aquatic life, leading to health risks for the population and economic losses. In Brazil, the CONAMA Resolution No. 357 of

2005 determines the five classes for fresh water in function of their intended uses, establishing quality standards for each of them. The Special Class assumes more noble uses, such as public supply and preservation of the natural balance of aquatic communities, and Class 4 represents the least noble uses. CONAMA Resolution No. 430/2011 establishes standards for the release of effluents into water bodies. In this way, both will be a fundamental reference for the development of this course module, especially in Chapter 3.

The main references used in the elaboration of this module were Piveli (2007) and CETESB (2016), in addition to those listed in Bibliographical References.

Chapter 1

Physical variables of water quality

The main water quality indicators used for physical characterization are: True Color, Conductivity, Solids Fractions, Transparency, Turbidity and Temperature.

a) True Color

The True Color of a water sample is associated to the degree of reduction in intensity that light suffers while passing through it, mainly due to the presence of dissolved solids, and of material in colloidal, organic and inorganic state. The color may come from natural sources (Figure 1), such as:

- Partial decomposition of vegetation (humic acid and fulvic acid) and
- Iron and manganese oxides naturally present in the soil.

Figure 1 - Color tone difference caused by natural sources in the merging of the Rio Negro with the Amazon River (Photo: A.Camolez, 2011).

Or anthropogenic

- Domestic sewage;
- Effluents from pulp and paper industries (lignin and cellulose), textiles (anilines) and tanneries.

It is important to differentiate the True (or Real) Color from the Apparent Color. (Figure 2):

The True (or Actual) Color is determined from a sample that has been filtered on a 0.45 µm membrane to remove suspended solids (those greater than 1 µm), since True Color is only associated with dissolved solids (less than 10-3µm) and part of the colloidal particles (intermediate size particles, between 1 and 10-3 µm), as shown in Figure 3.

The Apparent Color is the color that was measured in a sample that was not subjected to filtration, meaning a sample that contains suspended particles, both colloidal and dissolved.

Figure 2 - Procedure for determining color using the spectrophotometer at the CETESB Laboratory of Inorganic Chemistry Photo: R. Rossetti (2017)

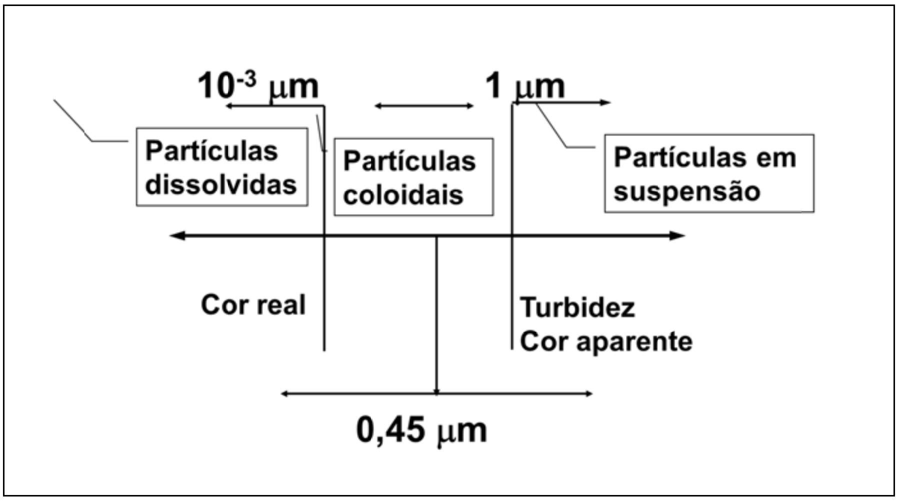

Figure 3 – Particle distribution in a sample of water.

Dissolved particles. Colloid particles. Particles in suspension.
Turbidity. Apparent Color. Real color.

Although determining the solids fractions does not clarify anything regarding the nature of the particles, it is practical and fast.

In the CETESB monitoring network, it is important to note that the coloration noted on the collection record basically consists of a visual observation made by the collection technician at the time of sampling. Coloration is a field parameter.

The variable's importance:

• Color causes aesthetic damage in public water supply (Figure 4). Thus, the limit established in Brazil by the Potability Standard (Ordinance No. 2914/2011 of the Ministry of Health) is 15 mg Pt-Co. L^{-1}.

Figure 4 – Negative esthetic effect of treated water (Available at: <http://avozdoportoal.blogspot.com.br/2015/01/agua-barrenta-continua-sem-solucao.html> Accessed in August of 2016).

- At Water Treatment Plants, color is a control parameter for the coagulation, flocculation, sedimentation and filtration processes.
- A reduction of light penetration into water bodies can cause ecological imbalances. Thus, in CONAMA Resolution No. 357/2005, the True Color limit for Class 2 water bodies is 75 mg Pt. L^{-1} (visual comparison: platinum-cobalt method).
- Color is a little used quality variable at Sewage Treatment Stations.

b) Conductivity

Conductivity is the numerical expression of the ability of water to conduct an electric current. It depends on ionic concentrations and temperature and indicates the amount of salts in the water column and therefore represents an indirect measure of the concentration of pollutants contained within fresh water.

Importance of variable:

In general, levels greater than 100 µS cm^{-1} indicate impacted environments. The conductivity also gives a good indication of the alterations in the composition of a type of water, especially in its mineral concentration, but it does not provide any indication of the relative amounts of the various components. The water's conductivity increases as more dissolved solids are added. High values may indicate the corrosive characteristics of that water. Brazilian legislation, CONAMA Resolution No. 357 of 2005, does not establish limits regarding conductivity.

c) Series of Solids

The total solids in a sample of water or effluent correspond to all the matter that remains as residue, after the water evaporates and dries using an oven set at 102 ° C. In general terms, the drying, calcination (550-600 ° C) and filtration operations are those that define the various solid fractions present in the water, which can be classified as follows:

- Physical Characteristics - Size:
    - Suspension
    - Colloidals
    - Dissolved
- Chemical Characteristics:
    - Volatile solids (organic)
    - Fixed solids (inorganic)

The methods used to determine the nine solids fractions are gravimetric, using an analytical or precision balance (Figure 5).

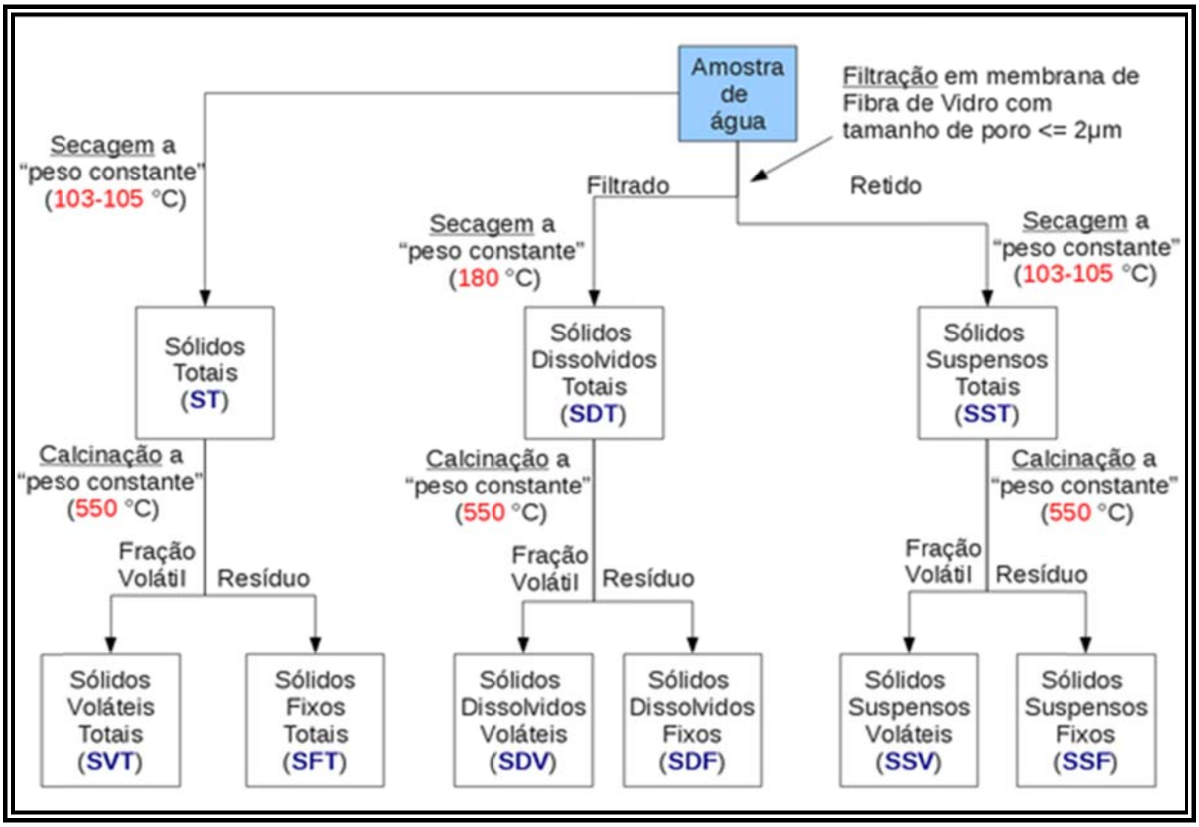

Figure 5 – Solids fractions (Available at: <http://www.c2o.pro.br/analise_agua/a1833.html> Accessed in August of 2016).

Sample of water. Filtration by glass fiber filter with <2um pore size. Retained. Filtered. Drying to constant weight. Total solids. Total dissolved solids. Total suspended solids. Total volatile solids. Fixed dissolved solids.

The variable's importance:

In the characterization of natural waters or of domestic and industrial effluents, the determinations of the concentrations of various solids fractions are not definitive regarding the behavior of the water or effluent in question, but it constitutes an important piece of preliminary information. It should be noted, for example, that although the concentration of volatile solids is associated with the presence of organic compounds in water, it does not provide any information about the specific nature of the different organic molecules that may be present. In addition, a portion of the organic molecules can initiate the volatilization process at temperatures other than the reference range of 550-600 ° C (maintained during the calcination step). Some organic compounds volatilize above 250 ° C, while others require, for example, temperatures in over 1000 ° C.

In addition to the nine solids fractions previously described, there is another important fraction called sedimentable solids. The determination of this fraction is performed using an Imhoff Cone, as shown in Figure 6. The unit is expressed in mL. L^{-1}.

Figure 6 – Imhoff Cone used to determine the amount of sedimentable solids at the CETESB Inorganic Chemistry Lab. Photo: C.L. Midaglia ,2017

For the water resource, sedimentable solids can cause damage to fish, causing their gills to clog up, and to other aquatic life. They can sediment in the river bed destroying organisms that provide food or might also damage areas of river beds used for fish spawning. The solids can retain bacteria and organic residues at the bottom of the rivers, promoting anaerobic decomposition. Thus, according to Decree No. 8468, the State of São Paulo has established two emission standards regarding this variable: 1mL. L^{-1}, to be released directly into the body of water (Article 18) and 20mL. L^{-1}, for release in the collecting network, provided with treatment (Article 19-A).

The dissolved solids fraction also has a quality standard regarding natural waters in Brazil. According to CONAMA Resolution No. 357 of 2005, for special water bodies the limit is 500 mg. L^{-1}.

d) Transparency

This variable is determined using the Secchi disk (Figure 7), which is immersed in the water to the depth where it is no longer visible. Thus, it is possible to determine the depth of the photic zone in lentic water bodies, in particular.

The variable's importance:

From the Secchi disk measurement, it is possible to estimate the depth of the photic zone in lakes or ponds, that is, the depth of vertical penetration of sunlight into the water column, which indicates the level of photosynthetic activity of lakes or reservoirs (Figure 8). Such depth is influenced by the concentration of suspended solids present in the water body.

Figure 7 - Secchi Disc (Available at: <http://www.corporacionsystemar.com/producto/138-disco.-secchi> Accessed in August of 2016)

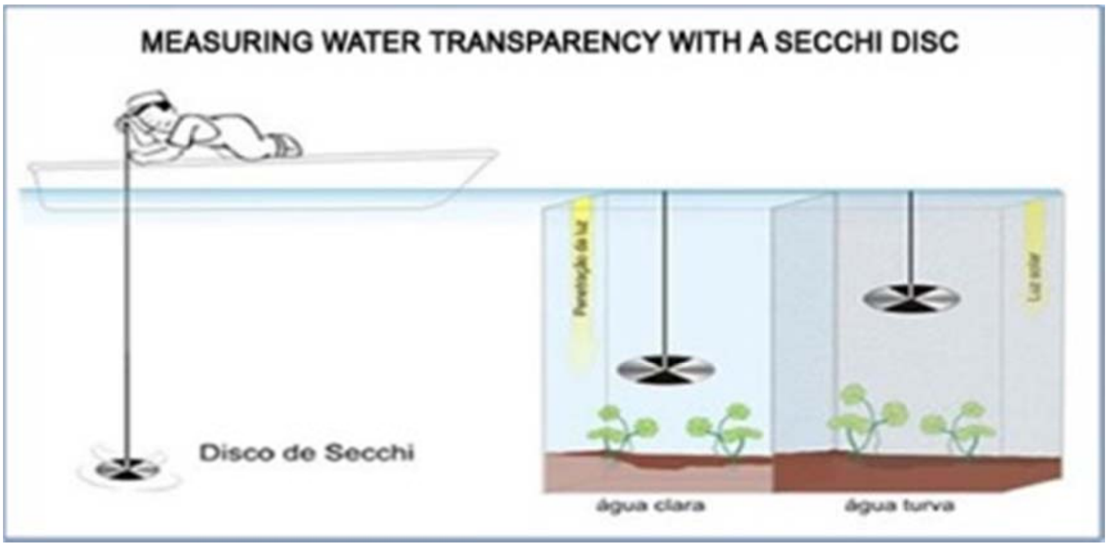

Figure 8 – Use of Secchi Disc (Available at:: <http://www.ebah.com.br/content/ABAAABdHEAE/parametros-qualidade-agua> Accessed in August of 2016).

e) Turbidity

The turbidity of a sample of water is associated with the degree of reduction in the intensity that light suffers when crossing it, due to the presence of suspended solids (those greater than 1 μm, according to Figure 3), which may be of natural origin, for example:

- Algae, organic waste, microrganisms

- Sand, silt and clay

Or of anthropogenic origin:

- Release of domestic sewage and industrial effluentsUrban drainage
- Erosive processes
- Mining activities

Although the Turbidity determination is not specific, since it does not indicate the composition of the particles, it is a practical and rapid determination.

The variable's importance:

- There is aesthetic damage of the public water supply. Thus, the limit established in Brazil, by Ordinance No. 2914/2011, of the Ministry of Health, is 5 UNT.
- In water treatment plants for public supply, it is an important variable in the control of coagulation, flocculation, sedimentation, filtration and disinfection processes (Turbidity can serve as a shelter for microorganisms, reducing the efficiency of disinfection).
- In natural waters, turbidity diminishes light penetration, hindering photosynthesis, which can reduce or suppress fish productivity, for example. Thus, in CONAMA Resolution No. 357/2005, the turbidity limit for Class 2 water bodies, for example, is 100 UNT.

f) Temperature

Temperature variations are part of the normal climate regime and natural water bodies exhibit seasonal and diurnal variations as well as vertical stratification as presented in Module I. Surface temperature is influenced by factors such as latitude, altitude, season, time of day and depth. Increased temperature in a water body is usually caused by industrial effluents (such as sugarcane industries) and thermoelectric and nuclear power plants.

Temperature plays a crucial role in the aquatic environment, conditioning the influence that several physical-chemical variables have. In general, as temperature rises from 0 to 30 ° C, viscosity, surface tension, compressibility, specific heat, ionization constant and latent heat of vaporization decrease while the thermal conductivity and vapor pressure increase. Elevations in temperature also decrease the solubility of gases in the water, increase the speed of physical, chemical and biological reactions and increase the rate of gas transfer, which can cause a bad smell.

The variable's importance:

- Maintaining aquatic life, since aquatic organisms have upper and lower thermal tolerance limits, optimal temperatures for growth, preference for certain thermal gradients and certain temperatures limitations for egg migration, spawning and incubation etc. Accordingly, CONAMA Resolution No. 357/2005 establishes the following as the emission standard: "temperature: less than 40º C, and the temperature variation of the receiving body must not exceed 3º C in the mixing zone".
- Temperature is considered to be an important variable in controlling the biological processes in water treatment.

Chapter 2

Chemical Variables of Water Quality

Some of the main chemical variables for indicating water quality are: dissolved oxygen, organic matter (BOD, DOC, COD and TOC), nutrients (nitrogen and phosphorus in their different forms), pH, metals (aluminum, manganese, iron, arsenic, barium, cadmium, chromium, copper, cobalt, lead, mercury, silver, nickel, selenium and zinc) chloride, total alkalinity, sulfate, hardness, fluoride, oils and greases, phenolic compounds, detergents, organochlorine pesticides, polycyclic aromatic hydrocarbons (PAHS), formation potential of trihalomethanes, polychlorinated biphenyls - PCBs and Emerging Pollutants.

a) Dissolved Oxygen

Oxygen from the atmosphere dissolves in natural waters due to the partial pressure difference. This mechanism is governed by Henry's Law, which defines the concentration of saturation of a gas in water, as a function of temperature:

$$CSAT = \alpha.pgás$$

Where:
α é uma constante que varia inversamente proporcional à temperatura e
pgás é a pressão exercida pelo gás sobre a superfície do líquido.
CSAT = α.p.
Where:
α is a constant that varies inversely proportional to temperature and
pgas is the pressure exerted by the gas on the surface of the liquid.
CSAT = α.p.

For example, oxygen makes up 21% of the atmosphere and, by Dalton's law, exerts a pressure of 0.21 atm. At 20 ° C, for example, α is equal to 43.9 and therefore the concentration of oxygen saturation in surface water is equal to 43.9 x 0.21 = 9.2 mg. L^{-1}. It is very common to find in the literature tables of oxygen saturation concentrations as a function of temperature, pressure and salinity of the water, as in the example in Table 1.

Table 1- Oxygen saturation content dissolved in fresh water at sea level, at different temperatures (in mg/L) (Derísio, 1992).

Temperature (ºC)	Altitude (m)				
	0	**250**	**500**	**750**	**1000**
0	14,6	14,2	13,8	13,3	12,9
2	13,8	13,4	13,0	12,6	12,2
4	13,1	12,7	12,3	12,0	11,6
6	12,5	12,1	11,7	11,4	11,0
8	11,9	11,5	11,2	10,8	10,5
10	11,3	11,0	10,7	10,3	10,0
15	10,2	9,9	9,5	9,3	9,0
20	9,2	8,9	8,6	8,4	8,1
25	8,4	8,1	7,9	7,6	7,4
30	7,6	7,4	7,2	7,0	6,7

The reintroduction rate of oxygen dissolved in natural waters through the surface depends on the hydraulic characteristics and is proportional to the velocity of the water body. Thus, the surface reaeration rate in a cascade (water fall) is greater than that of a river at normal velocity, which in turn presents a rate higher than that of a dam that normally has a low velocity.

Another important source of oxygen in water bodies is the photosynthesis of algae. This source is not very significant in the stretches of rivers that are downstream to areas where intense sewage is released. High turbidity and strong color make it difficult for the sun's rays to penetrate the water and only a few species that are resistant to severe pollution conditions can survive. Thus, the photosynthetic contribution of oxygen is only expressive after a large part of the bacterial activity in the decomposition of organic matter has occurred.

Dissolved oxygen is an important indicator of the pollution level in water bodies. In general, polluted waters are those with a low dissolved oxygen concentration (due to its consumption in the decomposition of organic compounds), while the clean waters show high dissolved oxygen concentrations, reaching a point slightly below the saturation concentration. The concentration of dissolved oxygen is directly proportional to the biodiversity found in any aquatic environment, Figure 9 serving as an example, since these concentrations may vary depending on water body conditions.

In a body of eutrophic water, however, the overgrowth of algae may influence the assessment of the pollution level when only the dissolved oxygen concentration is taken as the basis. A body of water with excessive growth of algae may have oxygen concentrations, during the day, well above 10 mg/L, even at temperatures above 20°C, characterizing a situation of super saturation. This mostly takes place in lakes of low water velocity, in which green crusts of algae may form on the surface (Figure 13). However, at night, the consumption of dissolved oxygen by algae can reduce the levels and cause fish mortality.

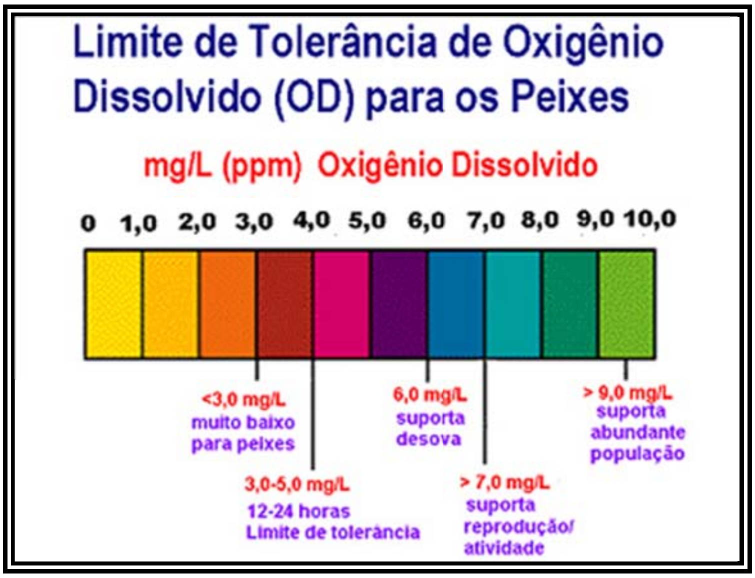

Figure 9- Dissolved oxygen concentration in relation to biodiversity (Available at: <http://www.quimlab.com.br/guiadoselementos/variaveis_quimicas.htm> Accessed in: August of 2016).
The fish tolerance limit for dissolved oxygen
Very low for fish/12-24 hours tolerance limit/withstands spawning/withstands reproduction/activity/withstands abundant population

b) Organic Matter

The greater the amount of biodegradable organic matter in the water, the greater the consumption of dissolved oxygen since aerobic microorganisms need oxygen to degrade it. Plant and animal organic matter and the microorganisms themselves are the main natural sources of organic matter. The anthropogenic sources of organic matter, not only biodegradable, are: domestic sewage, industrial effluents, and urban and agricultural drainage.

It can be said that there was a historical evolution in the determination of the organic matter in samples of water and effluents. In the beginning, the Volatile Solids were determined, then the Biochemical Oxygen Demand - $BOD_{5,20}$ and right after the Chemical Oxygen Demand - COD. $BOD_{5,20}$ and COD are indirect measures of the organic matter present in a sample, meaning that the results of these determinations are expressed in O_2/L mg. Finally, nowadays it is possible to directly determine the organic matter present in a sample, through Total Organic Carbon - TOC and Dissolved Organic Carbon - DOC.

- The Biochemical Oxygen Demand (BOD)

Biochemical Demand is the amount of oxygen required for microorganisms to degrade (oxidize) organic matter into a stable inorganic form. $BOD_{5,20}$ is normally considered to be the amount of oxygen consumed over a period of time, at a specific incubation temperature. A time period of 5 days at an incubation temperature of 20°C is often used and referred to as $BOD_{5,20}$. Thus, it indirectly indicates the organic matter content in the sewers or in the water body, therefore serving as an indication of the consumption potential of dissolved oxygen.

The largest increases of BOD in a water body are mostly caused by organic drainage. The presence of a high content of organic matter can induce the complete depletion of oxygen in the water, causing fish mortality and other forms of aquatic life.

According to CONAMA Resolution No. 357 of 2005, which establishes natural water classification standards, the $BOD_{5,20}$ limits for class 1, 2 and 3 water bodies are respectively 3, 5 and 10 mg. L^{-1}.

In the field of sewage treatment, BOD is an important parameter for controlling station efficiencies, regarding both aerobic and anaerobic biological as well as physical-chemical treatments (although oxygen demand only occurs in aerobic processes, the "potential" demand can be measured at the beginning and end of any type of treatment). In the CONAMA No. 430 of 2011, a minimum efficiency of 60% is required for the treatment process. This variable is also the basis for natural self-purification studies of water (Figure 10).

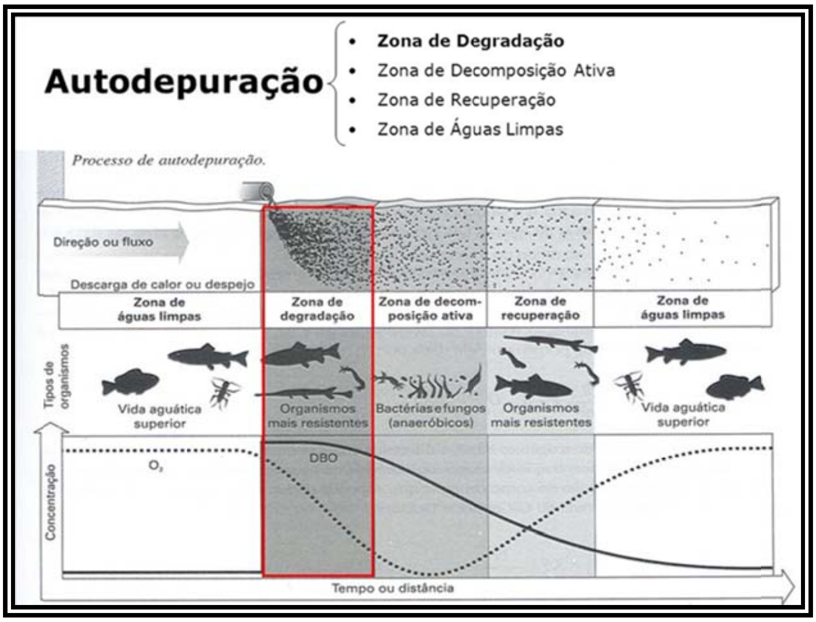

Figura 10- Self purification of a water body (Available at: <http://slideplayer.com.br/slide/358980/> Accessed on August of 2016)

Self purification/Degradation zone/active decomposition zone/recovery zone/clean water zone/flow direction/discharge of heat or disposal/types of organisms/concentration/superior aquatic life/more resistant organisms/bacteria and fungi/more resistant organisms/superior aquatic life/time or distance.

The BOD load expressed in kg/day is a fundamental parameter in the design of biological sewage treatment stations, giving form to the main characteristics of the treatment system, such as areas and volumes of tanks, the force of aerators, etc. The BOD load is the product of the effluent's water outflow through the BOD concentration. For example, in an existing industry, where a treatment system is to be installed, a program to measure outflow and analyze BOD can be established to obtain the load. The same can be done in an already installed sanitary sewage system. If that is not possible, estimated unit values may be calculated. Regarding sanitary sewage, it is traditional in Brazil to adopt a "per capita" contribution of $BOD_{5,20}$ of 54 $g.hab^{-1}.day^{-1}$.. However, a better definition of this parameter is necessary by determining the $BOD_{5,20}$ loads in drainage basins where the population is known. In the case of industrial effluents, it is also common to establish unitary contributions of $BOD_{5,20}$ as a function of units of mass or volume of processed product. Table 2 presents typical values of concentration and unitary contribution of $BOD_{5,20}$ for different types of effluents.

Table 2- Concentrations and loads of BOD in different types of effluents (Braile and Cavalcanti, 1993).

TYPE OF EFFLUENT	$BOD_{5,20}$ CONCENTRATION (mg / L)		UNITARY $BOD_{5,20}$ CONTRIBUTION (Kg/Day)	
	RANGE	TYPICAL VALUE	RANGE	TYPICAL VALUE
Sanitary sewage	110-400	220	---	54 g/hab.day
Bleached pulp (Kraft process)		300	29,2 a 42,7 kg/t	
Textile	250-600			
Dairy products	1.000-1.500		1.5-1.8 kg/m^3 leite	
Bovine slaughterhouse		1.12!		6,3 kg/1.000 kg live weight
Tannery (Cr)	2.500			88 kg/t salty skin
Brewery	1.611-1.784	1.718		10,4 kg/m^3 beer
Soft drinks	940-1.335	1.188		4,8 kg/m^3 soda
Citric juice concentrated	2.100-3.000			2,0 kg/1000 kg orange
Sugar and alcohol		25.000		

- Chemical Demand of Oxygen (CDO)

This is the amount of oxygen needed to oxidize organic matter in a sample by means of a chemical agent, such as potassium dichromate (Figure 11).

$$MO + Cr_2O_7^{2-}{}_{(aq)} + H^+{}_{(aq)} \leftrightarrow 2Cr^{3+}{}_{(aq)} + CO_{2(aq)} + H_2O_{(l)}$$

Figure 11- The reaction in determining CDO (Available at:<http://slideplayer.com.br/slide/9162028/> Accessed in August of 2016)

CDO values are normally larger than those of $BOD_{5,20,}$ with the test being done in less time. The increase in CDO in a water body is mainly due to waste from industries.

The COD is an indispensable parameter in the characterization studies of sanitary sewage and industrial effluents. COD is very useful when used in conjunction with BOD to observe the biodegradability of sewage. It is known that the oxidation power of potassium dichromate is greater than that produced by the action of microorganisms, except in very rare cases such as aromatic hydrocarbons and pyridine. Therefore, COD results for a sample are higher than those of BOD. As with BOD, only the biodegradable fraction is measured; the closer this value is to the COD, the more biodegradable the effluent is. It is common to apply biological treatments to effluents with $COD/BOD_{5,20}$ ratio of 3/1, for example. But very high values of this relationship indicate great chances of failure, since the biodegradable fraction becomes small, and the biological treatment is further impaired by the toxic effect on the microorganisms exerted by the non-biodegradable fraction.

The COD has been shown to be a very efficient parameter in the control of anaerobic sanitary sewage and industrial effluent treatment systems. After the growth in development that these systems had since the 70's, when new reactor models were created and many studies were conducted, it is observed the priority use of COD to control the applied loads and the obtained efficiencies. In these cases the BOD was only used as a secondary parameter, more to verify compliance with legislation since both federal and São Paulo state legislation does not include COD. It appears that the solids carried by the anaerobic reactors due to the rise of the gas bubbles produced or due to the flow bring greater deviations in BOD results than in COD ones.

Another important use of COD is in predicting sample dilutions in BOD analysis. Since the COD value is higher and the result can be obtained on the same day of collection, this variable can be used to signal the dilutions. However, it should be noted that the $COD/BOD_{5,20}$ ratio is different for the various effluents and that, for the same effluent, the ratio changes through treatment, especially when biological. Thus, a raw effluent with $COD/BOD_{5,20}$ ratio equal to 3/1, may, for example, be in the order of 10/1 after biological treatment, which acts to a greater extent on $BOD_{5,20}$.

- The Dissolved Organic Carbon (COD) and Total Organic Carbon (TOC)

The organic carbon, present in raw and waste water, consists of a variety of organic compounds in various states of oxidation. Some of these carbon compounds can be oxidized by biological or chemical processes, respectively providing biochemical oxygen demand (BOD) and chemical oxygen demand (COD). There are two types of organic carbon in the aquatic ecosystem: particulate organic carbon - POC and dissolved organic carbon - DOC. The TOC analysis considers the biodegradable and non-biodegradable portions of the organic matter, not receiving interference from other atoms that are bound to the organic structure, quantifying only the carbon present in the sample. Organic carbon in freshwater originates from living matter and is also a component of several effluents and sediments. Its environmental importance is due to the fact that it serves as a source of energy for bacteria and algae, in addition to forming complex metals. The part formed by the excreta of algae cyanophytes can, in high concentrations, become toxic, in addition to causing aesthetic problems. The total organic carbon in water is also a useful indicator of the level of pollution in the water body.

c) Nutrients (Nitrogen Forms and Phosphorus Forms)

Phosphorus and nitrogen are the main nutrients to be considered as indicators of the quality of fresh water. Both are called macro nutrients, since they are required in large amounts by the cells. Thus, they are essential parameters in programs for the characterization of industrial effluents that are meant to be treated through biological processes. Although it is a nutrient for biological processes, the excess of phosphorus in sanitary sewers and industrial effluents leads to processes of the eutrophication of the natural waters.

Phosphorus appears in natural waters, mainly due to discharges of sanitary sewage. Fecal organic matter and washing powder detergents used on a large scale are the main source. Some industrial effluents, such as fertilizers, pesticides, chemicals in general, canned foods, slaughterhouses, refrigerators and dairy products all provide excessive amounts of phosphorus. Drainage waters from agricultural and urban areas can also cause the presence of an excessive amount of phosphorus in natural waters.

As an example, in Brazil, the limit concentrations for total phosphorus in Class 2 water bodies, according to CONAMA No. 357, are:

- 0.030 mg. L $^{-1}$ for lentic water bodies,
- 0.050 mg. L $^{-1}$ for intermediates and
- 0.1 mg. L $^{-1}$ for lotic environments.

Phosphorus can occur in water in three different ways. Organic phosphates are the form in which phosphorus composes organic molecules, such as that of a detergent, for example. The orthophosphates are represented by the radicals, which combine with cations forming inorganic salts in the water and the polyphosphates, or condensed phosphates, orthophosphate polymers. This third form is not very important in studies of water quality control because it undergoes hydrolysis, rapidly becoming orthophosphates in natural waters.

Orthophosphates are bioavailable and, once assimilated, are converted into organic phosphate and condensed phosphates. After the death of an organism, the condensed phosphates are released into the water. However, they are not available for biological absorption until they are hydrolyzed by bacteria into orthophosphates.

With regard to nitrogen, the natural sources of this nutrient in natural waters are diverse. Sanitary sewage is, in general, the main anthropogenic source, introducing organic nitrogen into the waters due to the presence of proteins and ammoniacal nitrogen, by the hydrolysis of urea in the water. Some industrial effluents also contribute to discharges of organic and ammoniacal nitrogen into the waters, such as some chemical, petrochemical, steel, pharmaceutical, canned food, slaughterhouses,

slaughterhouses and tanneries. The atmosphere is an important source due to several mechanisms such as biofixation performed by bacteria and algae present in the water bodies, which incorporate the atmospheric nitrogen in their tissues, contributing to the presence of organic nitrogen in the waters; chemical fixation, a reaction that depends on the presence of light, also provokes the presence of ammonia and nitrates in the water, since the rain transports these substances, as well as the particles containing organic nitrogen to the water bodies. In agricultural areas, the drainage of rainwater through fertilized soils also contributes to the presence of several forms of nitrogen. Also in urban areas, rainwater drainage, associated with the deficiencies of the public sanitation, is a diffuse source of difficult characterization.

As seen, nitrogen can be found in waters in the forms of organic nitrogen, ammoniacal, nitrite and nitrate. The first two are reduced forms and the last two are oxidized. In this way, the degradation stages of organic pollution can be associated through the relationship between the nitrogen forms. In the areas of natural self purification in rivers, the presence of organic nitrogen in the degradation zone, ammonia in the active decomposition zone, nitrite in the recovery zone and nitrate in the clean water zone are noted (Figure 10). That is, if a sample of water is collected from a polluted river and the analyses show a predominance of the reduced forms then that means that the source of the pollution is nearby. If nitrite and nitrate predominate, sewage discharges further away.

Under current federal legislation, ammoniacal nitrogen is a classification standard of natural waters and the standard for sewage emissions. Ammonia is a toxin that greatly limits fish life, and many species cannot withstand concentrations above 5 mg. L^{-1}. Furthermore, as previously seen, ammonia provokes the consumption of dissolved oxygen in natural waters upon getting biologically oxidized, called second-stage BOD. For these reasons, the concentration of ammoniacal nitrogen is an important parameter for the classification of natural waters and is usually used in the constitution of water quality indices.

Nitrates are toxic and cause childhood methemoglobinemia, which is fatal for children (nitrate is reduced to nitrite in the bloodstream, competing with free oxygen, creating a blue blood). Therefore, nitrate is a standard of potability, with 10 mg. L^{-1} as the maximum value permitted by Ordinance No. 2914/2011 of the Ministry of Health.

When discharged into natural waters, the nutrients, especially phosphorus and nitrogen, present in the wastewater, cause the the environment to flourish, making it eutrophic. Eutrophication can facilitate a more intense growth of living things that use nutrients, especially algae. These large concentrations of algae can impede the varied uses of the waters, seriously damaging the public supply or causing pollution that occurs from the death and decomposition of these organisms.

The control of eutrophication, through the reduction of the nitrogen supply is compromised by the plurality of sources, many of which are extremely difficult to control, such as the fixation of atmospheric nitrogen, by some genera of algae. Therefore, it is preferable to control phosphorus sources.

It should also be remembered that the sewage treatment processes currently employed in Brazil do not normally include the removal of nutrients and the final treated effluents release high concentrations of these into the water bodies.

In biological reactors at sewage treatment plants, carbon, nitrogen and phosphorus must show up in the proportions that are adequate enough to enable cell growth without nutritional limitations.

In the treatment of sanitary sewage, these nutrients are found in excess, with no need to add them artificially, on the contrary, the problem regards how to remove. Some industrial effluents, such as those from paper and pulp industries, are basically composed of carbohydrates and contain almost no nitrogen and phosphorus. Thus, the these nutrients have to be added in order to achieve the recommended ratios, by using granulated urea, rich in nitrogen and ammonium phosphate that contains nitrogen and phosphorus, among other commercial products.

d) pH

PH represents the concentration of hydrogen H^+ ions, giving an indication of the acidity, neutrality or alkalinity of the water. Changes in pH can have a natural origin, such as the dissolution of rocks, the absorption of gases from the atmosphere, the oxidation of organic matter and photosynthesis, or anthropogenic, such as the release of domestic sewage and industrial effluents. Rivers may naturally have a low pH, as occurs with the main tributary of the Amazon River, the Rio Negro,

The variable's importance:

- pH variations on aquatic ecosystems may be direct due to the effects they have on the physiology of the species, or indirect, contributing to the precipitation of toxic metals, for example. Other conditions may exert effects on the solubility of nutrients. Therefore, in Brazil, the range of 6 to 9 has been established for all classes of natural water use, according to CONAMA Resolution No. 357.

- pH is found to be elevated in eutrophic bodies of water (Figure 12). In this condition, ammonia is largely present in NH3 free form, toxic to fish: According to the equilibrium, NH_3+H+ ↔NH+4, raising the pH of the water to a value between 11 and 12, Ammonium ion converts almost entirely to the gaseous form, NH_3.

- In Brazil, according to Ordinance No. 2914/11, the recommended pH of treated water should vary from 6.0 to 9.0, since acidic waters are corrosive and alkaline waters have an incrusting effect (Figure 13).

Bridge at the entrance of the city of Sabino, São Paulo.
Photo: C. L. Midaglia (2007)

Figure 12- Example of a eutrophicated water structure, with excessive algae growth (Arquives of the Banco Interáguas-CETESB).

Figure 13- Incrustation of a water pipe (Available at: <http://inspecaoequipto.blogspot.com.br/2013/08/inscrustacao-em-caldeiras.html> Accessed in August of 2016)

- PH also constitutes the standard for the emission of sewage and industrial liquid effluents, and the pH range of 5 to 9 has been established for the direct discharge into receiving bodies of water, according to CONAMA No. 430/2011.

e) Metals:

Aluminium

Aluminum and its salts are used as coagulants to treat water; as a food additive; in manufacturing cans, tiles, paper, aluminium; and in the pharmaceutical industry etc.

In water, metal can occur in different forms and is influenced by the pH, temperature and presence of fluorides, sulfates, organic matter and other binders. The concentrations of dissolved aluminum in neutral pH waters range from 0.001 to 0.05 mg. L^{-1}, but increase to 0.5-1 mg. L^{-1} in waters that more acidic or rich in organic matter. In highly acidic waters, affected by mining discharges, the concentrations of dissolved aluminum may be higher than 90 mg. L^{-1}. Some aluminum compounds, such as $AlCl_3$, may provoke toxicity in fish and other aquatic organisms.

In drinking water, the levels of this metal vary according to the source of water and to the aluminum-based coagulants that are used in the water treatment. US studies have shown that aluminum concentrations in coagulant-treated water ranged from 0.01 to 1.3 mg. treatment, with an average concentration of 0.16 mg. treatment.

The principal form of non-occupational exposure to aluminum for humans is through the ingestion of food and water. There are no indications that aluminum has acute oral toxicity, despite its widespread occurrence in food, drinking water and medicines. There is also no indication of carcinogenicity for aluminum. Ministry of Health Ordinance No. 2914/11 establishes a maximum permitted aluminum value of 0.2 mg. L^{-1} as an acceptance standard for human consumption (BRAZIL, 2011).

Iron

Iron appears mainly in groundwater due to the dissolution of the ore by the carbon dioxide of the water, according to the reaction:

$$Fe + CO_2 + \frac{1}{2} O_2 \rightarrow FeCO_3$$

In surface waters, the level of iron increases during rainy seasons due to sediment carriage, and the occurrence erosion processes along the margins.

Industrial effluents also play a role, since many metallurgical industries develop activities to remove the oxidized layer (rust) of parts before use through a process known as pickling, which is usually done by passing the piece through an acid bath.

The variable’s importance:

- Iron can cause the water supply to have a taste, odor and color, as well as stains on dishes and fabrics. Therefore, the limit is 0.3 mg. L^{-1} in the potability standard. It should be emphasized that the use of iron-based coagulants can cause an elevation in concentrations.
- In the treatment of water for public supply it is worth remembering that the presence of iron can influence the coagulation and flocculation phase. Iron-containing waters are characterized by high color and low turbidity. The flakes

formed are generally small, called "punctual", with very low settling velocities. At many water treatment plants, this problem is only solved by applying chlorine during what is called the pre-chlorination stage. Through the oxidation of iron by chlorine, the flakes become larger and easier to remove.

- In the treated water distribution network, there may be fouling and iron-bacteria formation, causing the biological contamination of the water in the network itself.
- Ferrous carbonate is soluble and often found in well water containing high levels of iron concentration.
- The effluent emission standard for dissolved iron in CONAMA Resolution No. 430/2011 is 15 mg/L.
- In the biological treatment of sewage, iron is an important nutrient, a builder of granules, flakes and biofilms.

Manganese

Manganese occurs naturally in both surface and groundwater, however, anthropogenic activities are also responsible for the increase in manganese concentrations in natural waters. Manganese and its compounds are used in the steel industry, metal alloys, batteries, glasses, oxidizing agents for cleaning, fertilizers, varnishes, veterinary supplements, among other uses.

Rare concentrations of manganese reach more than 1.0 mg/L in natural surface water and are normally present in concentrations of 0.2 mg/L or less.

The variable’s importance:

- Like Iron, it can cause taste, odor and color in the water supply. Thus, the limit established in the potability standard is 0.1 mg. L^{-1}.
- The effluent emission standard for Manganese in CONAMA Resolution No. 430/2011 is 1.0 mg. L^{-1}.

Toxic Metals

Toxic metals can be defined as those chemical elements that have an atomic number greater than 22, that have the property of being precipitated by sulfides and that have adverse effects on human health.

The main contribution of toxic metals to aquatic environments is of anthropogenic origin: industrial effluents (electroplating, chemical, smelting, tanning, etc.), mining, mining and agriculture.

The most relevant toxic metals are the following: Arsenic, Barium, Cadmium, Chromium, Copper, Cobalt, Lead, Mercury, Silver, Nickel, Selenium and Zinc.

The general importance of toxic metals:

- The toxicity of the metals happens within the aquatic community, for water users and for the micro-organisms responsible for treatment in sewage treatment plants

- Many toxic metals have a bioaccumulation effect (Figure 14).

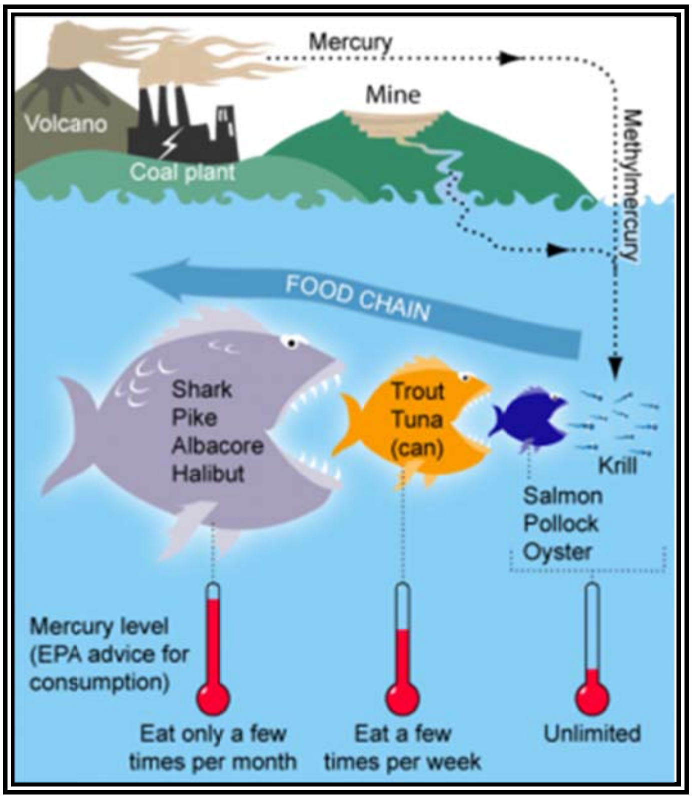

Figura 14--Bioaccumulation caused by Mercury (Available at: <http://scienceblogs.com.br/rastrodecarbono/2013/01/rastro-de-mercurio/> Accessed August of 2016)

- The effects on human health may range from local manifestations on the skin, on the lung membrane or in the intestinal tract to mutagenic, teratogenic and carcinogenic effects or even lead to death.

The specific importance of each of the toxic metals mentioned above may be found in Appendix D of the Surface Water Quality Report for the State of São Paulo in 2015 (CETESB, 2016).

f) Chloride

Chloride is the Cl- anion found in groundwater, arising from the percolation of water through soil and rocks. In coastal regions, through the so-called salt wedge intrusion (Figure 15), water with high levels of chloride is found.

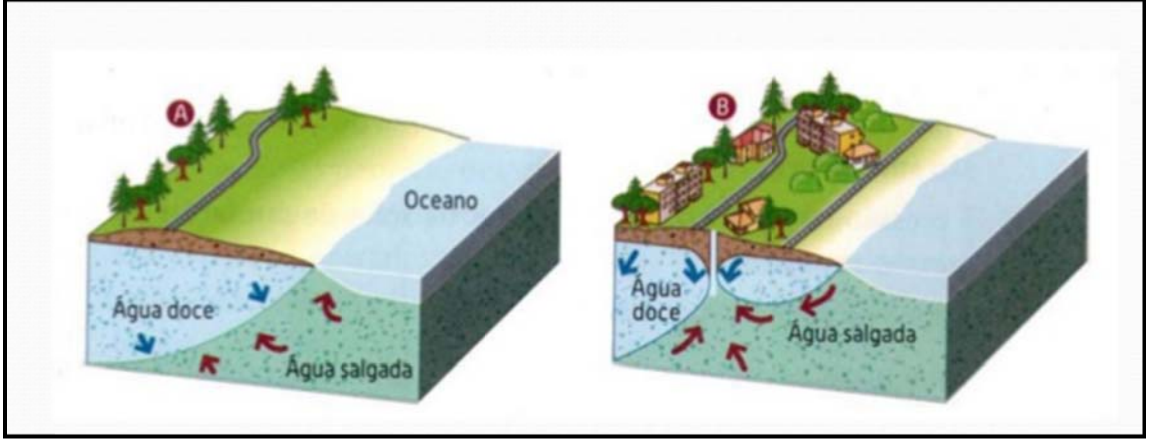

Figure 15- Salt Wedge Intrusion (B) (Available at: <http://www.tnh1.com.br/noticias/noticias-detalhe/meio-ambiente/250-mil-a-beira-do-colapso-crise-hidrica-avanca-degrada-reservas-e-cria-ilhas-de-desabastecimento-em-maceio/?cHash=ff51354ca59fe0f719d2a7d1e68a894f> Accessed in August of 2016).

Fresh water/salt water/ocean

In surface waters, the main sources of chloride are domestic sewage discharges, where each person eliminates around 4g of chloride per day through urine, representing about 90-95% of human excretions. The rest is expelled by feces and sweat (WHO, 2014). These quantities cause the sewage to have chloride concentrations that exceed 15 mg . L^{-1}.

There are also several industrial effluents with high concentrations of chloride such as the petroleum industry and some pharmaceutical, chemical and tannery industries.

In treated waters, the addition of pure chlorine or in solution leads to higher chloride levels resulting from the chlorine dissociation reactions in the water.

The variable's importance

- Chloride does not present toxicity to humans, except in the case of deficiency in the metabolism of sodium chloride, for example in congestive heart failure.
- The chloride ion provokes a salty taste to the water supply. Thus, the potability standard (Ordinance No. 2914/11) limits its concentration to 250 mg L^{-1}. However, the taste perception depends on the associated cation. In the case of calcium chloride, the flavor is only perceptible at concentrations above 1000 mg L^{-1}.
- O Chlorine causes corrosion in hydraulic structures, such as submarine oceanic outfall sewer systems, which have therefore been constructed with high density polyethylene (HDPE)
- Inhibition in anaerobic effluent treatment processes.

- Interferes with the determination of COD, and although this interference is reduced by the addition of mercury sulfate, the COD analyses of seawater do not present reliable results, so a TOC analysis should therefore be used.

- Can be used as an indicator of the presence of sewage in natural waters. Today, however, the thermotolerant coliform test is more accurate for this function.

- Chloride also has an influence on the characteristics of natural aquatic ecosystems, since they cause changes in the osmotic pressure of microorganism cells.

g) Total Alkalinity

The total alkalinity of a sample of water is a measure of the ability of the water to neutralize acids (ability to withstand changes in pH) due to the presence of carbonates, bicarbonates and hydroxides. Analytically, it is defined as the ability to quantitatively react with a strong acid up to a defined pH value.

The main components of alkalinity are the salts of carbonic acid, ie bicarbonates and carbonates, and hydroxides. Other salts of weak inorganic acids, such as borates, silicates, phosphates, or organic acids, such as salts of humic acid, acetic acid etc., also raise the alkalinity in water, but their effects are usually disregarded because they are not representative.

Bicarbonates and, to a lesser extent, carbonates, which are less soluble, dissolve in water due to their passage through the soil. Whenever the soil is rich in calcareous, the carbonic gas of the water solubilizes it, transforming it into bicarbonate, as shown in this reaction:

$$CO_2 + CaCO_3 + H_2O \leftrightarrow Ca\,(HCO_3)_2$$

The carbonates and hydroxides can appear in waters where algae blooms (eutrophic), and in a period of intense sunlight the balance of photosynthesis in relation to respiration is great and the withdrawal of carbon dioxide causes pH to rise to values reaching 10 units.

The main source of alkalinity of hydroxides in natural waters is the release of industrial effluents, where strong bases such as caustic soda and hydrated lime are used.

The variable's importance:

1. High concentrations of alkalinity in the public water supply can cause a bitter taste.

2. The distribution of slightly alkaline treated water is desirable for the formation of a thin layer of carbonate, which protects the net against corrosion. However, at high concentrations, it can cause fouling in water supply systems.

3. An important determination for water treatment and sewage treatment (buffering, resistance to a decrease in pH).

h) Sulfate

Sulfate is one of the most abundant ions found in nature. In natural waters, the source of sulfate occurs through the dissolution of soil and rocks and by the oxidation of sulfide. Anthropogenic sources of sulfate are domestic sewage and industrial effluents (pulp and paper, chemical etc.), the drainage of agricultural areas and the use of coagulants at water treatment stations.

The variable's importance:

- Sulfate causes problems due to its reduction of sulfide (under anaerobic conditions). In a sewage network where there are areas with a poor slope and , where organic matter accumulates, the sulfate can be transformed into sulfide, provoking the release of sulfhydric gas, which results in corrosion of the concrete sewage collectors and produces an odor, in addition to being toxic.
-
- In public water supply, sulfide may cause laxative effects. Thus, the sulfate limit established by Ordinance No. 2914/11 is 250 mg. L^{-1}.

- Can cause corrosion, toxicity and bad smells in sanitary sewage systems (collection and treatment). Thus, the limit for sulfate is 1,000 mg. L^{-1} for release into the network.

- During anaerobic treatment, it causes the inhibition of methanobacteria and the competition through the substratium (volatile acids).

i) Hardness

There are four main compounds that give water hardness: calcium bicarbonate, magnesium bicarbonate, calcium sulfate and magnesium sulfate.

The main cause of hardness in water is its passage through soil (dissolution of the calcareous rock by the carbonic gas in the water), according to the reactions:

$$H_2CO_3 + CaCO_3 \rightarrow Ca\ (HCO_3)_2$$

$$H_2CO_3 + MgCO_3 \rightarrow Mg\ (HCO_3)_2$$

In this way, it's more common to find a high level of hardness in groundwater than it is in surface water. The geological map of Brazil allows for the observation of regions that present soils with hardness characteristics such as in the Northeast, Central-west and Southeast, but the problem is much more serious in the United States and Europe, where many regions are subjected to very high degrees of hardness due to the composition of the soil there.

The hardness of a water can be perceived by its capacity to precipitate soap, that is, in hard waters, soaps become insoluble complexes, not producing any foam until the process is exhausted.

Hardness in water is defined by the presence of calcium and magnesium, mainly in addition to other cations such as iron, manganese, strontium, zinc, aluminum, hydrogen, etc., associated with carbonate anions (more properly bicarbonate, which is more soluble) and sulfate, As well as other anions such as nitrate, silicate and chloride.

The variable’s importance:

- The treated waters in conventional stations generally have a hardness that is a little higher than that of raw water due to the use of hydrated lime. Lime reacts with aluminum sulfate to form calcium sulfate. However, the amounts are relatively small relative to the levels of hardness that would provoke problems in the uses of the treated water.

- High concentrations in the public water supply can cause an unpleasant taste and have a laxative effect. It can also cause fouling in hot water pipes and reduce foam formation.

- Surface water pollution due to industrial activity is insignificant in relation to hardness, although the compounds that produce it are normally used in factories.

j) Fluoride

Fluorine is the most electronegative of all chemical elements. It is so reactive that it is never found in nature in its elemental form, mostly found in its combined form as fluoride. Fluorine is the 17th most abundant element found in the earth's crust with a representation of 0.06 to 0.9% and occurring mostly in the form of fluorite (CaF_2), fluoroapatite ($F_{10}(PO_4)_6$) and cryolite (Na_3AlF_6). However, in order for there to exist an availability of free fluoride, for example biologically available fluoride, ideal soil conditions and other minerals or other chemical components and water must be present. Fluoride traces are normally found in natural waters and high concentrations are usually associated with underground sources. In places where there are fluoride-rich minerals, such as near high mountains or areas with geological deposits with a marine origin, concentrations of up to 10 mg. L^{-1}or more are found. The highest concentration of fluoride in natural waters is 2,800 mg. $L^{-1,}$ in Kenya.

Some industrial effluents also release fluoride into natural waters, such as glass industries and electricity-conducting wires.

Other sources of fluoride are toothpastes, chewing gums, vitamins and medicines. Fluoride ingested through water is almost completely absorbed by the human body, whereas the fluoride in food is not fully absorbed. Once absorbed, fluoride is rapidly distributed through the human body, much of it is retained in the bones, while a small part is retained in the teeth. Fluoride can be excreted through the urine and its elimination depends on a number of factors such as the person's state of health and their degree of exposure to this substance.

Fluoride is added to the public water supply in order to offer protection against cavities in teeth. Fluoride reduces the solubility of the mineralized part of the tooth, making it more resistant to the action of bacteria and inhibiting enzymatic processes that dissolve the organic protein substance and the calcifying material of the tooth. However, the fluoridation of water must be done using strict control, using good dosing equipment and implementing effective fluoride residual control programs in the water supply network. According to studies carried out in the United States, concentrations of fluoride above 1.5 mg. L^{-1} increase the incidence of dental fluorosis. Ordinance No. 2914/11 of the Ministry of Health establishes a maximum value for fluoride of 1.5 mg. L^{-1} in drinking water.

k) Óils and Greases

Oils and greases are organic substances of mineral, vegetable or animal origin. These substances are usually hydrocarbons, fats and esters, among others. They are rarely found in natural waters, usually coming from industrial waste and disposal, domestic sewage, effluents from mechanical workshops, gas stations, and the drainage from public roads. Industrial disposals are the ones that most contribute to an increase of greases in water bodies, among them refineries, refrigerators, soaperies, etc.

Oils and greases, according to the analytical procedure used, consist of the set of substances that can be extracted from the sample by using a certain solvent and that does not volatilize during evaporation of the solvent at 100 ° C. These substances, soluble in n-hexane, comprise fatty acids, animal fats, soaps, greases, vegetable oils, waxes, mineral oils etc. This parameter is usually also identified by MSH - material soluble in hexane.

The low solubility of oils and greases is a negative factor regarding their degradation in waste treatment plants using biological processes and oils and greases cause problems in water treatment when present in water sources used for public supply. The presence of fatty material in the water bodies can cause asphyxia in the fish, since it adheres to the gills. It also causes aesthetic problems and reduces the area of contact between the surface of the water and the atmosphere, preventing the transfer of oxygen from the atmosphere to the water.

In their decomposition process, oils and greases reduce dissolved oxygen, due to the elevation of $DBO_{5,20}$ and COD, causing damage to the aquatic ecosystem. Brazilian legislation recommends that oils and greases be absent from class 1, 2 and 3 water bodies.

l) Phenolic Compounds

Phenols and their derivatives appear in natural waters through the discharge of effluents from industries working with rubber processing, glues and adhesives, impregnating resins, electrical (plastic) and steel components.

Phenols are toxic to humans, aquatic organisms and the micro-organisms that are part of sewage treatment and industrial effluent treatment systems.

Resolution No. 430/11 of CONAMA stipulates a limit of 0.5 mg L^{-1} for total phenols in effluents discharged into water bodies. In natural waters, the standards for phenolic compounds are quite restrictive, from 0.003 mg L^{-1} of total phenols in class 1 or 2 water bodies, for example.

When present in the natural waters of a spring, the phenols react with the free chlorine used in the treatment for public supply forming chlorophenols that cause a foul taste and odor in the water.

m) Detergents (Surfactants or Tensioactive substances that react with Methylene Blue)

Analytically, meaning according to the recommended analytical methodology, detergents or surfactants are defined as compounds which react with methylene blue under certain specified conditions. These compounds are referred to as "methylene blue active substances" (MBAS) and their concentrations are relative to the straight chain alkyl benzene sulfonate (LAS), which is used as the standard in analysis.

The source of the detergents found natural waters is mostly domestic sewage, which have 3 to 6 mg . L^{-1} of detergents, and the detergent industry, which releases liquid effluents with about 2000 mg. L^{-1} of the active principle. Other industries, including those processing metal parts, employ special detergents that have a degreasing function.

The variable’s importance:

The indiscriminate discharge of detergents into natural waters leads to negative aesthetic impacts due to the formation of foams (Figure 16). One of the most critical cases of foam formation occurs in the municipality of Pirapora do Bom Jesus, in the state of São Paulo. Located on the banks of the Tietê River, downstream of the São Paulo Metropolitan Region, it receives the city’s sewage, largely without treatment. The existence of rapids leads to the release of foams that continuously form layers above the river bed that have at least 50 cm. Then due to winds, the foam spreads over the city, biologically contaminated as the foam impregnates itself onto the surface of the soil and other materials, making them oily.

Figure 16- Photo of foam forming on the São Pedro Hydroelectric Power Plant, in Itu. (C.L. Midaglia, 2015).

Additionally, detergents can exert toxic effects on aquatic ecosystems. The straight linear alkyl benzene sulfonates (LAS) has progressively replaced the branched chain alkyl benzene sulfonates (ABS) because it is considered biodegradable. In Brazil, this substitution occurred at the beginning of the 1980s and although standard biodegradability tests have been developed, this effect is not yet known in a safe way. Toxicity tests with aquatic organisms have been improved and there is a tendency to be more widely used in pollution control programs.

Detergents have also been blamed for the acceleration of eutrophication. Most of the commercial detergents employed have phosphorus in their formulations and they are also known to exert a toxic effect on zooplankton, a natural predator of algae.

n) Chlorinated and Organochlorinated Pesticides

Pesticides can consist of inorganic substances, such as sulfur, mercury, fluorine etc. Since these pesticides are highly toxic, they have been replaced by synthetic organic pesticides classified as chlorinated or organochlorinated, pyrethrins, phosphorous, chlorophosphorous and carbamates.

Chlorinated pesticides such as DDT, HCH, Aldrin and Lindane have long residual effect. Most compounds are hydrophobic but have a high solubility in hydrocarbons and fats. Organochlorine pesticides have a low acute toxicity, but present chronic toxicity problems due to their capacity for accumulation along the food chain and in biological tissues.

Currently, the use of organochlorines is prohibited or restricted because due to its low degradation rate in the environment. Many of the pesticides are on the list of 12 Priority Organic Pollutants, such as Aldrin and DDT. This group of pollutants is characterized as being highly toxic to living organisms and bioaccumulative. They are resistant to chemical, biological and photolytic (light) degradation and affect human health and ecosystems even in small concentrations.

The affinity of pesticides for adsorption in suspended mineral matter and organic colloids is important for understanding their mobility in water bodies.

Contamination by organochlorine pesticides occurs through the skin, oral and respiratory exposure, which can attack the central nervous system, causing sensory disturbances in balance, behavioral changes and involuntary muscular activity, among others. In cases of inhalation, cough, hoarseness and hypertension may occur.

o) PAH (Polycyclic aromatic hydrocarbons)

Polycyclic aromatic hydrocarbons are a class of semi-volatile organic compounds, formed by linearly or angularly connected benzene rings, containing only carbon and hydrogen in their structure. Of the polycyclic aromatic hydrocarbons, sixteen are names by the United States Environmental Protection Agency as being priority pollutants. They have been carefully studied due to their toxicity, persistence and predominance in the environment: acenaphthene, acenaphthylene, anthracene, benzo(a) anthracene, benzo(a) fluoranthene, benzo(a) pyrene, benzo(k) fluoranthene, benzo(g, h, i) perylene, chrysene, dibenzo (a, h) anthracene, phenanthrene, fluoranthene, fluorene, indene (1,2,3-cd) pyrene, naphthalene and pyrene.

The behavior, transport and destination of these compounds in the environment depend on their physicochemical and biochemical characteristics. Usually PAH's are persistent in the environment and have a low solubility in water, with the exception of naphthalene, which is relatively soluble. In most cases, this solubility decreases with an increase in the number of ring and with the molecular weight of the compound. This is one of the most important properties regarding the transportation of these compounds in the environment. The more water soluble compounds are more easily transported since they tend to have a low adsorption in the soil particles. Additionally, they are more susceptible to biodegradation due to their simpler structure.

PAHs can cause toxicological effects on the growth, metabolism and reproduction of the entire population of plants and animals (microorganisms, terrestrial plants, aquatic life, amphibians, reptiles, birds and mammals). These effects may be associated with tumor formation, acute toxicity, bioaccumulation and the skin damage of various animal species. The main research themes of these compounds have been their carcinogenic, mutagenic and genotoxic properties.

CONAMA Resolution No. 357/2005 establishes limits for several PAHs in water bodies, as it also does for indene (1, 2, 3-cd) pyrene, of 0.05 µg/L.

Ministry of Health Ordinance No. 2914/11 does not establish a maximum value for PAHs in drinking water, but adopts the standard of 0.7 μg/L for benzo [a] pyrene (BRAZIL, 2011), a value also recommended by the WHO.

p) Trihalomethames Formation Potential (THMFP)

The use of non-specific variables to evaluate the efficiency of a treatment system as well as the water quality of a particular spring is a common practice in Water Treatment Stations. The turbidity parameter, for example, is widely used in WTSs for the control and operational monitoring of particulate material removal. The color and density of thermotolerant coliforms are other variables of this type that are commonly used. These non-specific variables can be a valuable tool for an initial evaluation of water quality characteristics in water sources that are intended for public supply. They can also be very useful for quickly verifying changes in water quality during treatment processes.

Concerning the formation of light organochlorine compounds (such as chloroform), the so-called trihalomethanes, during the chlorination process, it becomes necessary to evaluate the source regarding the amount of precursors of these compounds.

The use of the trihalomethane formation potential as a non-specific parameter of the THM precursor measurement can be used to compare the quality of several raw water sources with potential for supply with the possibility of producing elevated concentrations of THMs in treated water during treatment and distribution processes. Ordinance No. 2914/11 of the Ministry of Health establishes a maximum value of total trihalomethanes of 0.1 mg. L^{-1} as the acceptance standard for water for human consumption.

q) Biphenyl-polychlorates (BPCs)

Biphenyl-polychlorates generically refer to the class of organochlorine compounds that result from the reaction of a biphenyl group with anhydrous chlorine in the presence of a catalyst. They are also part of the Priority Organic Pollutants (POPs). Many substitutions may take place in BPC molecules regarding the number chlorine atoms, which may vary from 1 to 10. Up to 209 different structures may be obtained and these are called **BPC** congeners.

BPCs were used worldwide and on a large scale mainly in transformers and electric capacitors and to a lesser extent in heat transfer fluids and as additives in the formulation of plasticizers. In Brazil, there are no records of the BPC production, since the product was always imported from the United States and Germany.

BPCs may enter the environment by accident or loss during handling, through the volatilization of components contaminated by BPCs, leakage in transformers and capacitors, irregular storage, smoke from the incineration of BPC-containing products and from the disposal of industrial effluents into rivers and lakes.

The aquatic environment is an important environment for the accumulation of BPCs, which get incorporated through the discharge of industrial effluents. In sediments, BPCs are usually adsorbed into the organic matter, and sorption-desorption processes represent a determining factor in the mobilization of BPCs into the water column.

Toxicological studies have shown that contamination from BPCs may provoke alterations in the reproductive functions of organisms, causing disturbances in sexual maturation and teratogenic effects. In the environment, these effects may propagate along the trophic chain through bioaccumulation. Human exposure to BPCs might lead to symptoms such as chloracne, hyperpigmentation, eye problems, and elevated liver and gallbladder cancer mortality rates. The maximum value for BPCs stipulated in CONAMA Resolution No. 357/2005 for water bodies is 0.001 mg L^{-1}.

r) Emerging Pollutants

Emerging pollutants have been reported as endocrine disruptors or having the potential to deregulate the body.

Some of these compounds affect biota by causing reproductive dysfunctions and studies indicate they may also induce cancers. Regarding humans, although conclusive cause-and-effect relationships have not yet been established, several studies indicate the possibility that disorders such as birth defects, behavioral and neurological alterations, immunological deficiency, accelerated puberty, reduced semen quality and cancers are related to emerging pollutants with endocrine disrupting action.

These pollutants can be divided into the following groups:

- Pesticides: Atrazine, lindane, triclosan, DBCP (dibromochloropropane), PCP (pentachlorophenol), rifuralin;
- Natural steroids: Androgens, estrogens, phytoestrogens;
- Drugs: Fluoxetine, tamoxifan, fluvastatin, medetomidine, propranolol, synthetic hormones
- Industrial chemicals: Alkylphenols, phthalates, bisphenol-A, styrene, brominated flame retardants (PBDEs), surfactants (including perfluoroctanesulfonates - PFOS)•

Since the effects of these pollutants are still not completely understood, these contaminants are not normally included in routine monitoring plans of the environmental or health quality control bodies nor are they included in regulations or legislation.

Chapter 3

I. Types of diagnosis: emergency care, monitoring activities, trend analysis, impact assessment, analysis of compliance with legal standards

Understanding the importance of all the water quality indicators is essential in order to properly interpret the results obtained during the analysis of raw water, treated water or effluent samples. Such understanding allows us to correctly define and evaluate the interest parameters, which indicate significant changes in water quality, making it possible to carry out adequate diagnoses in different situations.

II. Emergency Care

According to CETESB's Chemical Emergency Information System (CEIS), 365 chemical accidents were registered in 2015, and in approximately 16% of the cases the aquatic environment got affected, and its quality was altered (Figure 17)

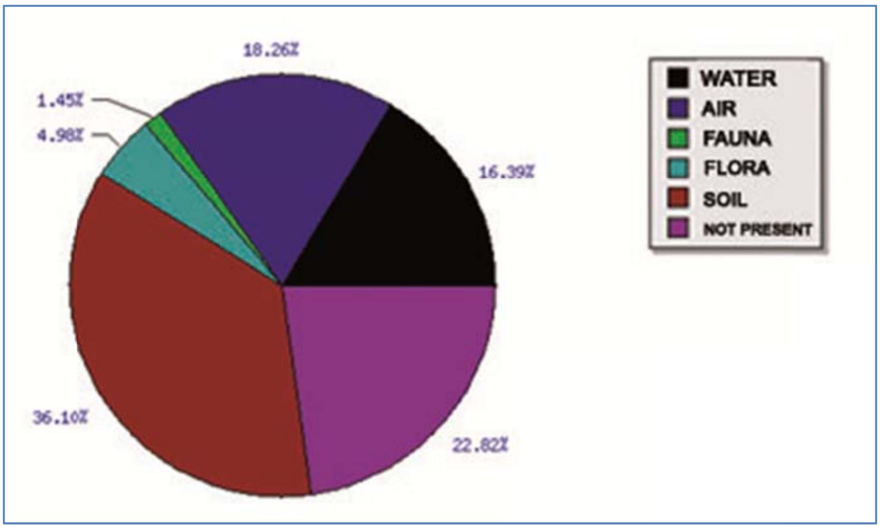

Figure 17 – Graph of the environments affected by chemical emergencies treated by the CETESB in 2015 (SIEQ, 2017).

In the State of São Paulo, CETESB is also the institution that deals with cases that involve fish mortalities. Such cases mostly derive from alterations in the water quality, such as reduced concentrations of dissolved oxygen or reduced pH. However, it is not always possible to identify the causes or the sources of contamination provoking such changes. In 2015, there were 148 cases of fish mortality or other aquatic organisms.

The graph in Figure 18 shows the evolution in the number of cases of fish mortalities from 2010 to 2015, according to the vocation of the Unit of Management of Water Resources - UGRHI (Agriculture/farming, In industrialization, Industrial and Conservation). The highest number of cases registered in 2014 can be explained by the drought observed in that year.

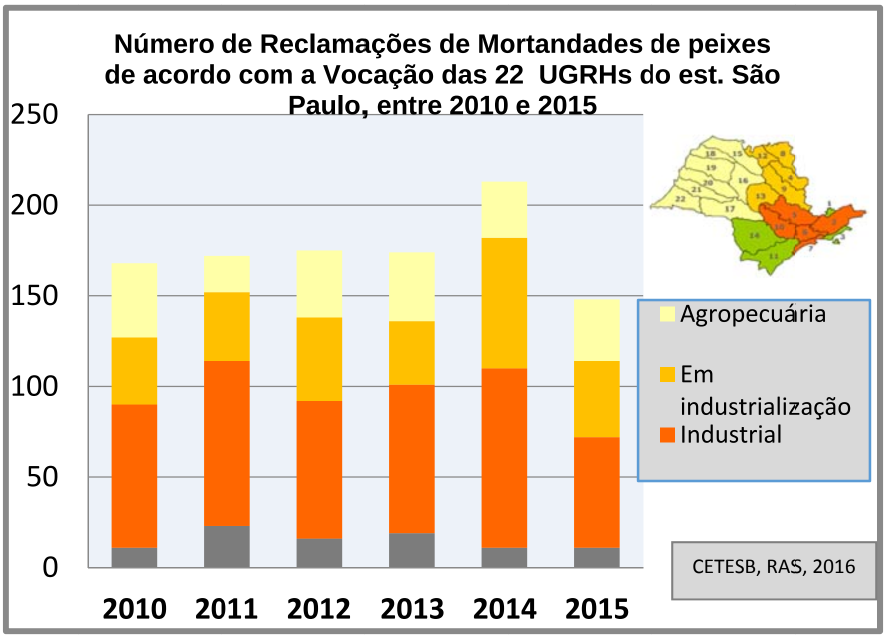

Figure 18 – Evolution in the registered cases of fish mortalities from 2010 to 2015 (CETESB, 2016).

Number of complaints of fish mortalities according to the 22 UGRH in the state of Sao Paulo, between 2010 and 2015. Agriculture/In industrialization/Industrial/Conservation

The causes of fish mortalities registered in 2015 were identified in 76% of the cases, and were due to a low concentration of dissolved oxygen, the presence of contaminants such as domestic sewage and toxic substances, and the blooming of potentially toxic algae or cyanobacteria (Figure 19).

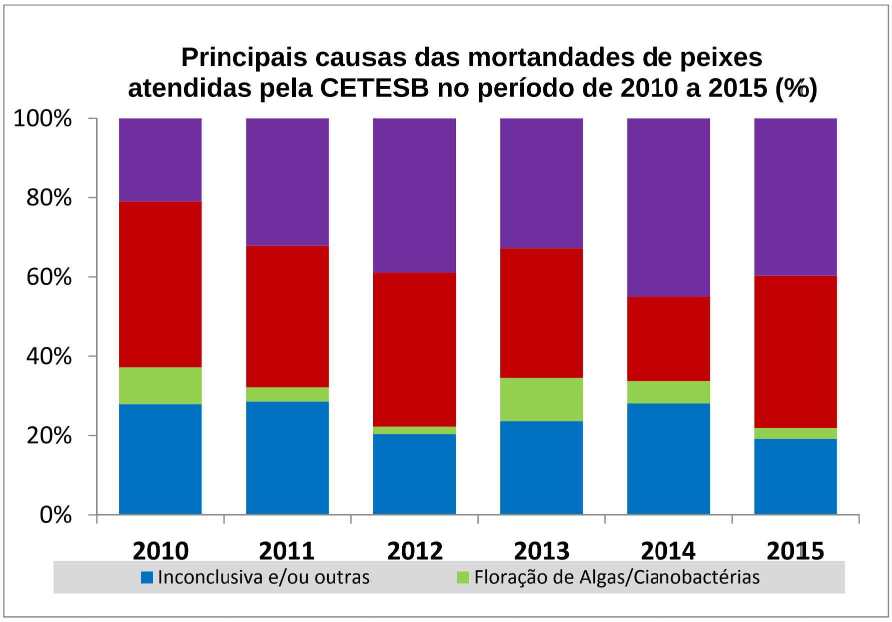

Figure 19 – Proportion between the causes of fish mortality from 2010 to 2015, dealt with by CETESB (CETESB, 2016).

Main causes of fish mortality attended to by the CETESB from 2010 to 2015 (%) Inclusive and/or others/algae blooming/cyanobacteria/contamination/ low DO

Whether or not a fish is killed, any emergency (accidental spillage of products or the discharge of effluents outside the standards established by CONAMA Resolution No. 357 of 2005) must be addressed as quickly as possible in order to identify the intensity of the alterations provoked in the water and take the appropriate control measures.

III. Monitoring Activities

The main monitoring activities regarding the quality of the water bodies are the analysis of the conformity of the effluents released according to the current legal standards and the verification of the directing of effluents and rainwater toward the appropriate drainage networks.

Adequate routing of effluents and rainwater within an industry or other business is important in order to protect water bodies and effluent treatment systems. This is because, in Brazil, a separator system has been adopted, which separates the rainwater in independent drainage lines. These are not directed to Sewage Treatment Plants, but to surface water bodies. Only effluents are directed towards treatment systems. However, there are countries that adopt the combined system, which is the one in which rainwater is sent along with the sewage to the Sewage Treatment Plants (Figure 20).

Figure 20 - Separated and combined sewage systems (Von Sperling 2005).

Separator system/sewage network/rain water network/W.T.P./combined system/sewage and rainwater network W.T.P

Thus, the monitoring of industries or other businesses must verify that rainwater is getting properly routed, meaning that if it does not come into contact with any type of industrial effluent then the rainwater should be adequately routed to the rainwater drainage network. If rainwater flows through industrial areas, coming into contact with contaminants such as oils and greases then it should be directed to the sewage system that is connected to a treatment system, the industry itself or the responsible concessionary.

Regarding the analysis of compliance of the effluents that are released, CONAMA resolutions No. 357 of 2005 and 430 of 2011, address the classification of water bodies and the conditions and standards for effluent release in Brazil, respectively. The industry, or other business that manages liquid effluents, must meet both the water quality standard according to its classification and the emission standard. For example, effluent and water body samples must be collected during the monitoring. In the water body, samples should be collected upstream from the sources of pollution, which may also be diffuse (Figure 21), and downstream of them, taking into account the extent of the mixing zone. According to CONAMA Resolution No. 430 of 2011, the mixing zone is defined as the region of the receiving body, which is estimated based on theoretical models accepted by the competent environmental agency, that extends from the effluent release point and is delimited by the surface in which a balance of mixing between the physical and chemical parameters is achieved, as well as a biological balance between the effluent and receiving body, being specific for each parameter. Concentrations of substances that are not in accordance with the established quality standards for the recipient body may be allowed provided they do not compromise the intended uses of the water body.

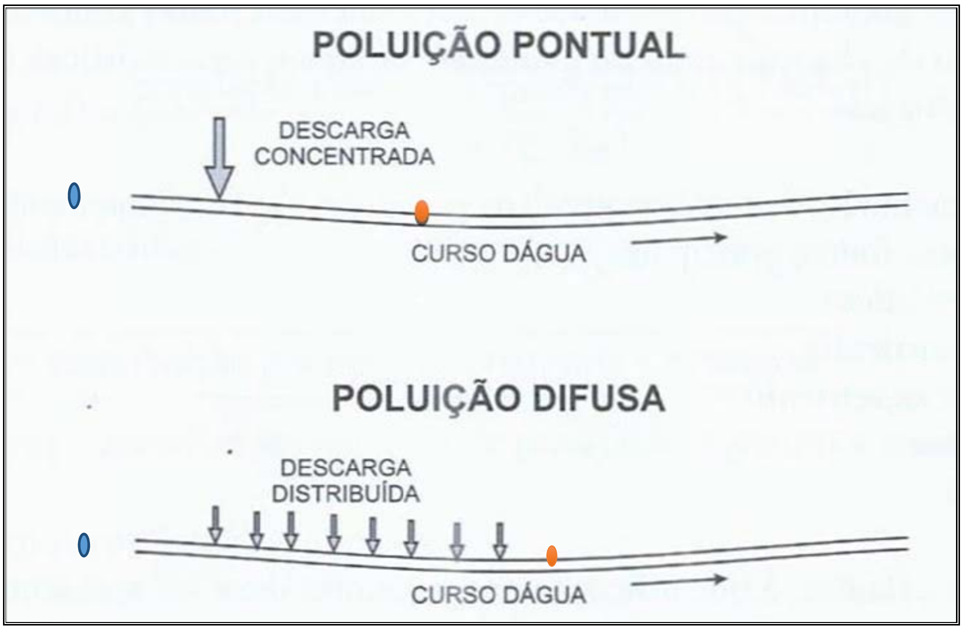

Figure 21 – Point and diffuse pollution sources and examples of points for water samples (adapted from Von Sperling 2005).

Point pollution/concentrated discharge/watercourse/diffuse pollution/distributed discharge/watercourse

IV. Trend Analysis

Freshwater quality evaluation is complemented by temporal and spatial analyses that allow for the configuration of trends regarding analyzed parameters. The temporal analysis of a water body makes it possible to identify the most critical stretches in terms of water quality change.

For example, the 2007 CETESB Inland Water Quality Report (CETESB, 2008) presented a study that allowed for the evaluation of the effectiveness of the Tietê River Clean-up Project, which has been in operation since 1992. The methodology adopted for the spatial evaluation took into consideration the means of the quality variables $BOD_{5,20}$, ammoniacal nitrogen, total phosphorus, nickel and zinc, relative to 2007, and for the temporal evaluation the annual averages of the previous ten years were used, making it possible to calculate the trend by Linear Regression Analysis. The bar color shows the variable's tendency along the last ten years: green (improvement), red (deterioration), yellow (unchanged) and gray (uncalculated) (Figure 23-27).

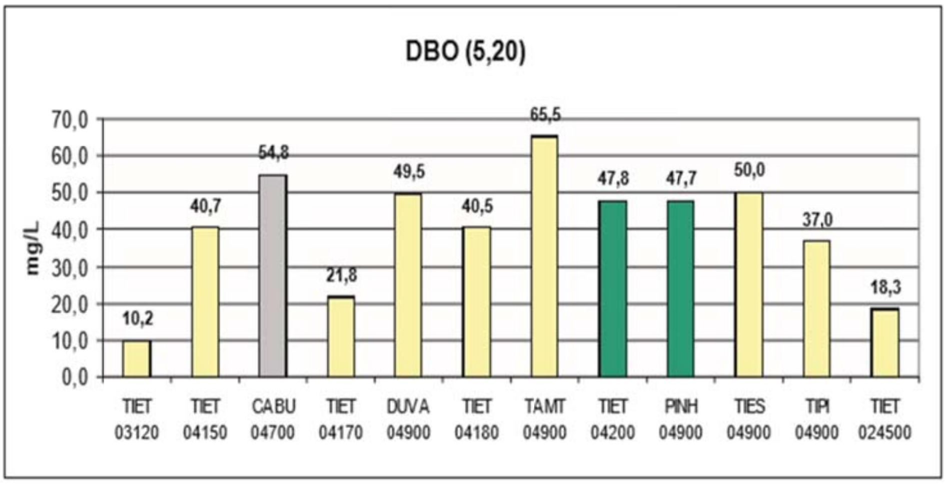

Figure 22 – Average of $BOD_{5,30}$ (2007) and the tendency over the previous 10 years (CETESB, 2008).

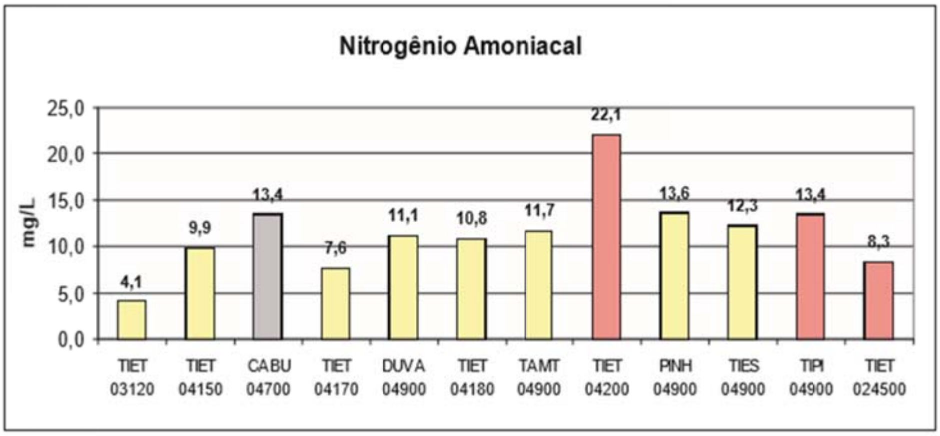

Figure 23 – Average of ammoniacal nitrogen (2007) and the tendency over the previous 10 years (CETESB, 2008).

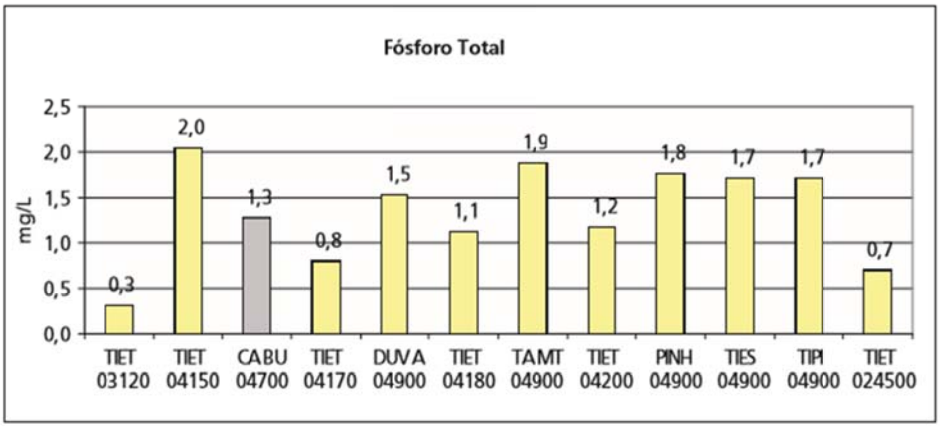

Figure 24 – Average of total phosphorus (2007) and the tendency over the previous 10 years (CETESB, 2008).

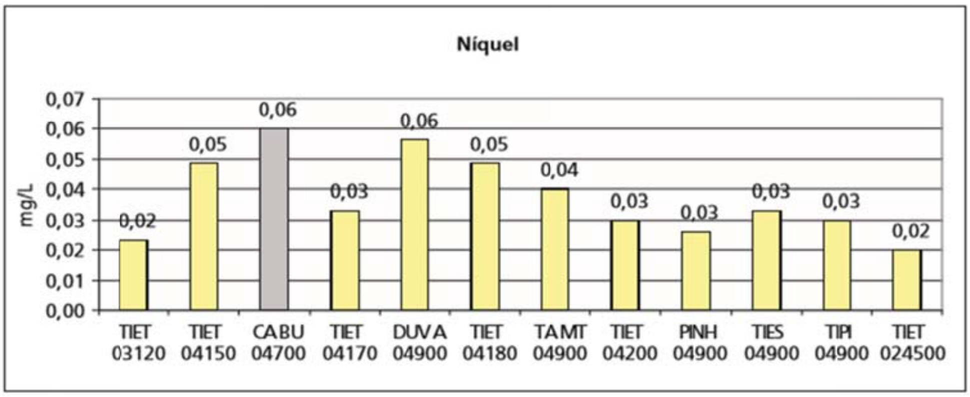

Figure 25 - Nickel (2007) and the tendency over the previous 10 years (CETESB, 2008).

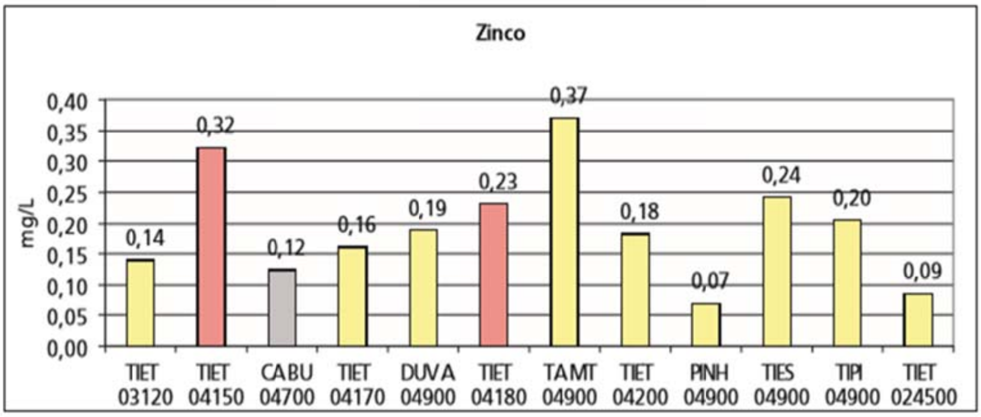

Figure 26 – Zinc average (2007) and the tendency over the previous 10 years (CETESB, 2008).

The Tietê River, along most of its passage through the Alto Tietê Basin, is stipulated as a Class 4 water body by State Decree No. 10.755/77 and, therefore, has no established maximum limits for the analyzed variables. However, changes in the values of these variables in space and time made it possible to evaluate the behavior of water bodies in relation to environmental sanitation actions.

V. Impact Assessment

The change in water quality is a negative environmental impact resulting from several types of actions, such as industries, roads, landfills, sewage treatment plants, and especially in the construction and operation stages of any of these projects.

In a matrix for the identification of potential impacts for transmission line projects and for electrical substations, it is possible to consider the potential impact as the changes in surface water quality during the pre-construction, construction, post-construction and operation stages.

Following the activities of an environmental impact study, basic studies, or an environmental diagnosis, it is possible to gather the information needed in order to identify and predict the impacts of an enterprise for its subsequent evaluation. In assessing the water quality of a river, one should take into account its seasonal variation, both for the preparation of a sampling plan and for the collection of secondary data. In Figure 28, hypothetical, one can observe the natural behavior of an environmental parameter over time. If the baseline study's elaboration does not consider the seasonal variation, the value of T1 can be used as a reference and the value of T2 as an impact can be overvalued..

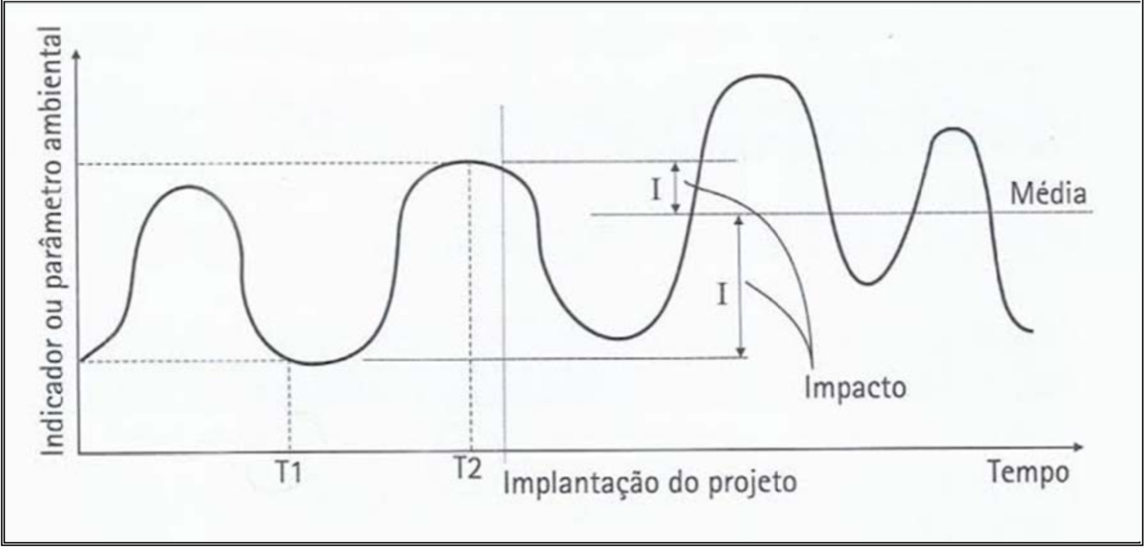

Figure 27 - Hypothetical example a quality parameter's variation throughout time (SANCHEZ, 2006).

Environmental indicator or parameter/Project implementation

VI. Analysis of compliance with legal standards

In accordance with the intended uses, CONAMA Resolution No. 357 of 2005 discriminates the waters of the national territory in fresh waters, which are those that have salinity below 0.05%, brackish waters, with salinity between 0.05% and 3%, and saline waters, which present salinity greater than 3%.

With respect to freshwater, there are 5 classes established by CONAMA Resolution No. 357: Special Class, Class 1, Class 2, Class 3 and Class 4, with the Special Class being the one that presupposes nobler uses, such as supply for human consumption and preservation of the natural balance of aquatic communities, and Class 4, which foresees less noble uses. The classification of watercourses can be understood as the establishment of the water quality goal to be reached or maintained in a water body according to intended uses. In this video produced by ANA it is possible to better understand the objectives of water body classifications.

For each of the classes, there is an established quality level to be achieved or maintained for each water body that guarantees the intended uses. The quality is assessed based on compliance with the limits established by the resolution for each quality parameter, from the conventional ones, such as dissolved oxygen, turbidity and biochemical oxygen demand, to toxic contaminants ones, such as pesticides and metals. CONAMA Resolution No. 357 of 2005 also establishes standards for the release of effluents, which was then complemented and modified by CONAMA Resolution No.430 of 2011.

Compliance with quality standards and release standards aims at to preserve water bodies. When releasing an effluent into a body of water, the launching standards and standards of the receiving body must be met according to its classification. If the effluent meets the release standards but not the receiving water quality standards, then the environmental agency should establish more restrictive limits for the effluent.

In addition to CONAMA resolutions No. 357 and 430, state and municipal laws should always be consulted, as they may establish more restrictive limits or contain additional parameters, such as the COPAM/CERH-MG Joint Normative Ruling of May 2008, which establishes limits for Total Suspended Solids, a parameter not included in the CONAMA Resolution.

Questions:

1) In your country, is there any law, resolution or regulation that establishes classifications of water bodies? How many and what are the classes?

2) What are the minimum limits established for dissolved oxygen? Are they expressed in mg L or % of saturation?

3) With regard to organic matter, Brazilian legislation establishes a limit only for the BOD. In your country, is there also a limit for COD, TOC or DOC?

4) Are there cases in your country of bodies of water that have naturally high levels of color and turbidity? What are the causes of these occurrences?

5) In your country, are there also water bodies that naturally have high or low pH values in relation to the range established by legislation?

6) In your country is there a concern with the formation of trihalomethanes during the water treatment processes for public supply? Is there any control in the source, such as the evaluation of the trihalomethane formation potential? And in treated water, is there a limit to these compounds?

7) With regard to total phosphorus, in your country's legislation, are different limits established that take into account the type of aquatic environment: lotic or lentic?

8) What are the variables that make up the WQI used by CETESB? Is this index also used in your country?

9) Regarding seasonality, how is the rainfall regime in your country?

10) Specify an occurrence of fish mortality that has took place recently in your country. Check what actions were taken and whether the cause was identified.

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