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Water Stress Induced by Enrichment of Nutrient and Climate Change Factors

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Abstract

Human activities accelerate the rate of water, air, and soil environment degradation. In this paper, we propose to present the effects of important stressors for water bodies, represented by continuous enrichment with nutrients and climate change. Nutrients' concentration increases especially nitrogen and phosphorus, associated with temperature increases and extreme weather events, involve important physical, chemical, and biological alterations of water quality. The effect of the stressors' factors can be seen on the main parameters which characterize water: temperature, pH, dissolved oxygen, transparency, chlorophyll *a*, nitrogen and phosphorus compounds, and plankton population. The main changes which occur in the water reservoirs consist of modifications of taste and odor, increased acidification, decreased transparency, oxygen depletion, increased toxicity, increased sediments quantity, excessive growth of phytoplankton, and macrophytes vegetation. The water quality of lakes, streams, and estuaries can be assessed using the trophic status that can be described mainly using limiting nutrients' concentrations (N total, P total), primary productivity (chlorophyll *a*), and Secchi disc parameters, and also the Carlson's index that includes all of these.

Keywords: eutrophication, stress factors, nitrogen, phosphorus, climate change, temperature, dissolved oxygen, transparency, chlorophyll *a*, trophic status assessment, Carlson's index

1. Introduction

Water has a unique place on the planet as it supports life on the earth. Clean water is an important resource for drinking, irrigation, industry, transportation, recreation, fishing, hunting, the biodiversity support, and sheer aesthetic enjoyment.

The main water stressors are human activities reflected by nutrients' inputs and climate change by increasing temperature and extreme weather phenomena. Nutrients, especially phosphorus and nitrogen from various sources, and increasing temperature are the major causes of degradation of the aquatic ecosystems, namely eutrophication.

Eutrophication can be a natural process in surface waters occurring as they age through geological time, over hundreds or thousands of years or it can be very fast when the nutrients are present in high concentrations, due to anthropogenic activities and climate change [1, 2].

Degradation of these vital water resources (coastal areas, lakes, and reservoirs all over the world) can be measured by the loss of natural systems, followed by the modification of the trophic chains with their component species, and the increase in the number of individuals of a species in preference to others [3].

It is considered one of the major forms of water stress, which is extremely variable being influenced by the specific characteristics of sites such as nutrient stoichiometry, biodiversity, climate-related factors (temperature, precipitation, and storming), and the basin geomorphology [4, 5].

The main sources of nutrients (nitrogen and phosphorus), its effect on water quality associated with influence of climate change factors, are presented in this chapter. The stressors' effects, nutrients, and climate exchange were highlighted by the parameters: temperature, pH, Secchi disc (SD) transparency, chlorophyll *a* (CHL), dissolved oxygen (DO), total phosphorus (TP), total nitrogen (TN), and plankton populations. The trophic stage was assessed using temperature, limiting nutrients concentrations (N total, P total), and their ratio TN/TP, primary productivity (chlorophyll *a*), and transparency (Secchi disc) parameters, and also the Carlson's index that includes all of these. To illustrate how one can achieve a surface water quality evaluation was presented using the trophic status of Lake Snagov, Romania, assessment.

2. Water stressors

Human activities accelerate the degradation rate of water, air, and soil. Continuous enrichment with nutrients and climate change are important stressors for water bodies. Increasing nutrients' concentrations associated with increasing temperature and extreme weather events involve important changes in the physical, chemical, and the biological configuration of the waters' characteristics [6].

2.1. Nutrient inputs

2.1.1. Sources of nutrients

The main stressors that influence the water quality and trophic chain reaction are macronutrients, such as phosphorus (P), nitrogen (N), silicon (Si), and micronutrients such as potassium (K), sulfur (S), calcium (Ca), magnesium (Mg), iron (Fe), and molybdenum (Mo) are also

needed. N, P, and K are considered primary nutrients, and N and P are the major limiting nutrients in most aquatic environments [6–8].

The nutrient inputs in natural water body by both point and disperse sources. The point sources may be wastewater effluents (domestic and industrial) — most importantly, runoff and leach flows from waste disposal systems, infiltrations from animal feedlots, unsewered industrial sites runoffs, sanitary sewers overflows, runoff from constructions sites, erosion into the lake. The most important dispersed (nonpoint) sources are leachate of synthetic and natural fertilizes from agriculture parcels and forest, runoff and infiltration from animal feedlots, runoffs from agriculture/irrigation, pasture and range, urban runoff from not-sewered areas, septic tank leachates, and atmospheric deposition on water surface [1, 10].

The results of enrichment of nutrient consist in the increase of aquatic primary production and lead to visible algal blooms causing high turbidity and increasing anoxia in the deeper parts, thus increasing the acidity and the modified aquatic ecosystems [9–11]. All these involve the water quality deterioration, drinking water treatment problems, and decrease in the perceived aesthetic value of the water body. The physical and chemical properties of the water influence the distribution and trophic dynamics in the water body. Depending on the content of nutrient and the production of organic materials, the water can have a trophic (degradation) level lower or higher.

2.1.2. Water trophic level classification

According to the content of mineral nutrients, and the effect of these on primary production, the trophic level classifications of water can be characterized using the terms as follows [12–14]:

- *oligotrophic*, poor in nutrients (nitrogen, phosphor) — nutrient deficient, small production of organic matter — primary production (amount of organic carbon produced by photosynthesis), clear waters, well illuminated, well oxygenated, low algae production, diatoms predominant;
- *mesotrophic*, medium levels of nutrients, intermediate level of primary production, clear water, and ponds with beds of submerged aquatic plants;
- *eutrophic*, more nutrients, primary production, and higher organic compounds, the oxygen concentration decreases with depths and the deep water layer is anoxic during summer, development of microalgae and cyanobacteria, weak illuminated due to microalgae bloom;
- *hypertrophic*, greatly excessive nutrient inputs, excessive primary production, the oxygen concentration decreases with depths and the deep water layer is anoxic, slow illuminated, higher turbidity, fish killing possible in summer and under winter ice.

2.2. Climate change

2.2.1. Introduction

Both natural and human factors change the earth's climate. The natural factors which cause the changes in climate are the modifications in the earth's orbit, alterations in the solar activity,

or volcanic eruptions. Since the Industrial Revolution began around 1750, human activities have contributed substantially to climate change by adding greenhouse gas emissions including water vapors (H_2O), carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and several others which have caused the earth's surface temperature to rise. Atmospheric CO_2 concentrations have increased by more than 40% since preindustrial times, from approximately 280 parts per million by volume (ppmv) in the eighteenth century to 396 ppmv in 2013. **Figure 1** shows the variations of the atmospheric CO_2 , CH_4 , N_2O per year [7, 16].

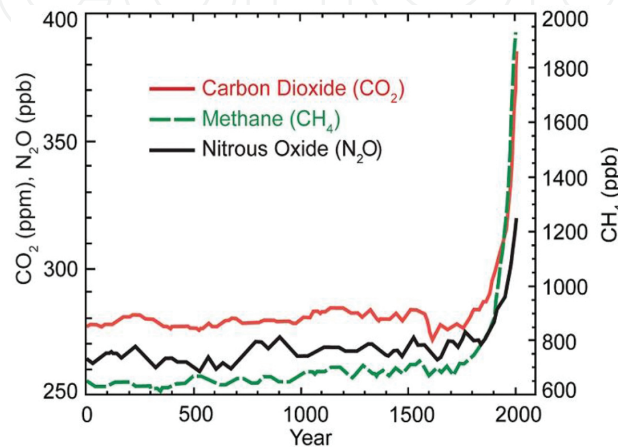


Figure 1. Atmospheric CO_2 , CH_4 , N_2O variations per year [7].

2.2.2. Effect of climate change

Freshwater resources are vulnerable to climate change; warming of the climate system increases global average air and influences the hydrological cycle [17]. Climate change associated with the water cycle (**Figure 2**) includes water body and land temperature increase [18], accelerated glaciers melting, decreasing the surface of water and land occupied with snow, increased evaporation and level of lakes water reduction, increased level of coastal marine and ocean and inundation, wetland loss by sea level rise, changes in the seasonal distribution and amount of precipitation, increasing precipitation intensity sometimes as extreme weather—storms, changes in the balance between snow and rain, increasing nutrients' concentration by soil washing and soil erosion [19], increasing acidity in rivers, lakes, seas, and oceans [20]. **Figure 2** shows the conceptual diagram visualizing the main components of climate change and their major effects on freshwaters [21].

Waters with similar effect filters, however, should respond similar to climate variability. Hydrodynamic patterns are influenced largely by the depth and size of the lake affecting the annual heat budget, temperature stratification during summer and winter, the concentration of oxygen in the hypolimnion, salt solubility, and availability of nutrients. The retention time (a factor depending on morphometry and through-flow) determines if internal or external processes dominate.

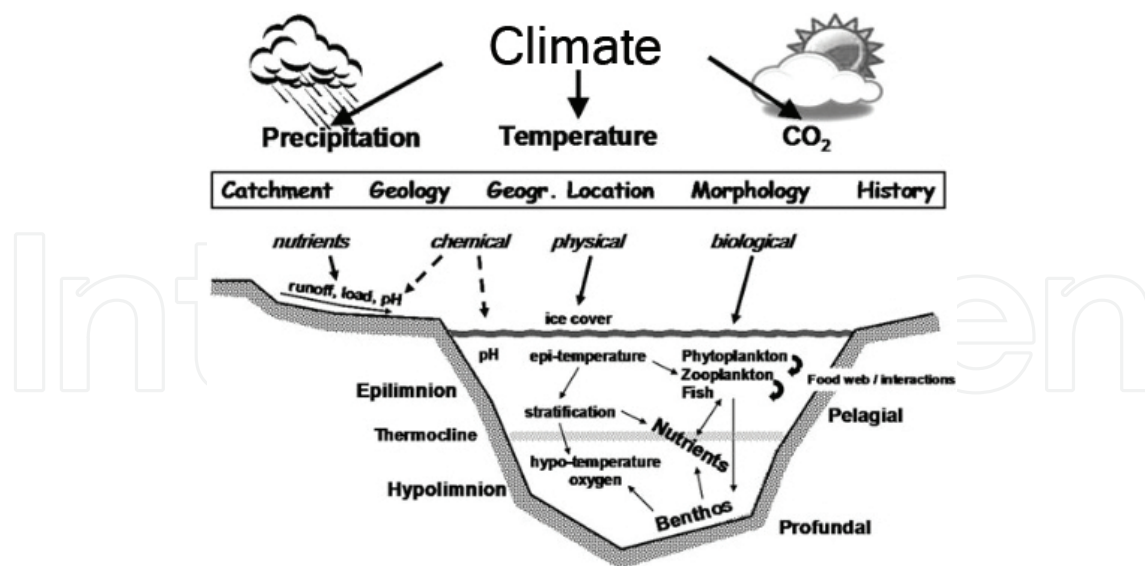


Figure 2. Conceptual diagram visualizing the main components of climate change and their major impacts on freshwaterers [21].

Warming of the atmosphere will lead to warmer and wetter winters, and hotter and drier summers. Large quantities of precipitation are expected in winter and spring which will come down as rain rather than snow. The flow regime in stream and rivers changes reaching the maximum flow faster than usual. Larger runoffs combined with more frequent extreme rainfalls may result in floods, increased erosion, and wash out of nutrients, which ultimately lead to the eutrophication of rivers and lakes.

In subtropical and tropical regions, storms and floods occur during rainy seasons. In temperate zones, the summer temperatures increase, the stream and river flow decrease, and the period of thermal stratification extends. In the warmer lakes, the oxygen is less available because the solubility of this element declines with increasing temperature. Decreasing oxygen concentration with increasing temperature and increasing the decomposition rates of organic compounds will increase the consumption of oxygen, which may lead to deoxygenating in deeper parts of lakes. In glaciated regions, the discharge will first increase due to more melt water and later decrease when glaciers have disappeared [19, 22, 23].

3. Stressors' effect on eutrophication characteristics parameters

The stressors' effects can be well highlighted by the mains parameters: temperature, pH, Secchi disc transparency (SD), chlorophyll *a* (CHL), dissolved oxygen (DO), total phosphorus (TP), total nitrogen (TN), and plankton populations [24].

3.1. Temperature and aquatic stratification

Usually, the atmospheric temperature influences the temperature of natural water bodies and these two together depend on the geographical location and meteorological conditions

(rainfall, humidity, wind velocity, etc.). The water temperature varies with depths, at the surface the temperature is higher than at greater depths, a phenomenon known as aquatic stratification. The water temperature influences the chemical, physical, and biological processes. Gas solubility decreases with increase in temperature, and biochemical activity doubles every 10°C of temperature increase. Thus, this kind of heating may cause a thermal impact on receiving water bodies and may influence the whole native community [25, 26].

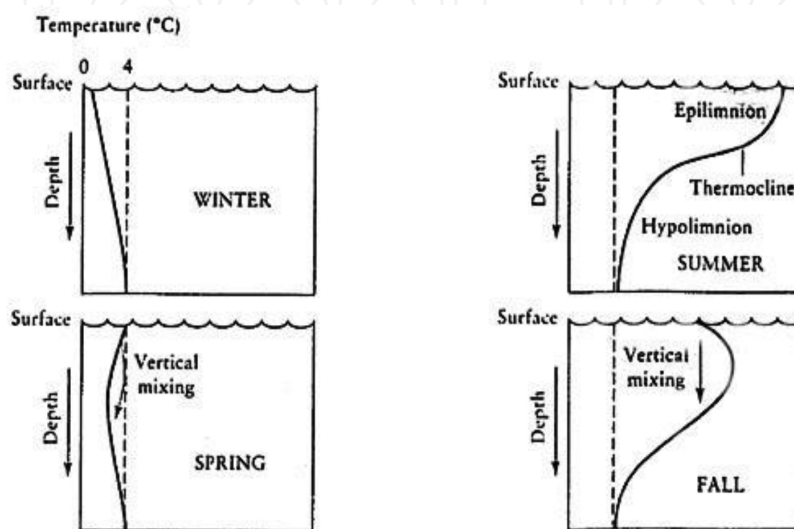


Figure 3. Temperate lakes are thermally stratified in the summer but mix each spring and autumn [28].

Because the lakes and reservoirs are deep enough, they stratify, generating “layers” of water with different physical characteristics. The large differences in density between layers of water determine thermal stratification. The density is influenced by temperature, so at about 3.98 °C the water is most dense (heaviest). The water stratification is seasonal. In the spring time, in temperate climates, immediately after the ice melts, the surface water begins to warm to 0°C. The increasing density of the warming water along with wind cause this surface water to sink and mix with the deeper water, a process called spring turnover. In this period, the water column is cold and has approximately the same temperature (**Figure 3**). During the late spring and summer, the sunlight is absorbed in the water column, heating up with the air average daily temperature increases. In the absence of wind, temperature decreases exponentially with the depth. The lake is now stratified into three layers of water, termed summer stratification. The upper layer, called the epilimnion zone, is in contact with the atmosphere and seasonal climate factors variations, is warm, well-mixed, has a higher pH and higher dissolved oxygen. The thermocline is a plane where the greatest water temperature changes and is very resistant to wind mixing. Hypolimnion starts beneath the epilimnion, extending to the lake bottom, is the coldest layer of a lake in summer, and the warmest layer during winter, usually dark, receives insufficient irradiance (light) for photosynthesis to occur and relatively undisturbed. In deep, temperate lakes, the bottom-most waters of the hypolimnion are typically close to 4°C throughout the year [26, 27].

Epilimnion is cooling down during autumn when decreasing the difference of the density to the hypolimnion. When the temperature of surface and bottom waters and density are approximately the same, winds can mix the entire lake. In winter, the surface water is cooling until it freezes; thus it appears less distinct density stratification because the density difference between 0 and 4°C water is quite small; most of the water column is isothermal at a temperature of 4°C, which is denser than the colder, lighter water just below the ice [26, 29].

Blue-green algae tend to dominate warmer waters while green algae do better under cooler conditions. The toxicity of unionized ammonia is also related to warmer temperatures [30]. The maximum specific growth rate is in the range 5–40°C for members of the Chlorophyta and Bacillariophyta [31]. The optimal temperature for phytoplankton cultures is generally between 20 and 24°C, most commonly cultured species of microalgae tolerate temperatures between 16 and 27°C [32].

3.2. pH

The pH value is a measure of water acidity or alkalinity and the number expresses the concentration of hydrogen ions indirectly and is expressed to the pH scale (measured on a scale of 0–14). Water pH changes are governed by the amount of free CO₂, carbonates, and bicarbonates and are accompanied by the changes in other physicochemical aspects that in turn influence the quality of water. Algal and macrophytes mass increase by the photosynthesis act, the CO₂ increase, in dissolved state, as results of the respiration processes and decomposition of organic matter, reduce the pH [33].



The buffering system CO₂/HCO₃⁻/CO₃²⁻ maintains pH around the neutral level. Depending on the current pH level operates these equations in both directions. When pH increases Eqs. (2) and (3) shift to the right.

The presence of high alkalinity (>100 mg/l) represents considerable buffering capacity and reduces the effects of both photosynthesis and decay in producing large fluctuations in the pH [30].

A minor change in the pH of water determines increasing solubility of phosphorus and other nutrients—making them more available for plants. Increasing accessible nutrients' quantity, determine increasing demand for dissolved oxygen and creates a eutrophic lake where other organisms living in the water become stressed.

The properly pH range for most fish is between 6.0 and 9.0 with a minimum alkalinity of 20 mg/l, with ideal CaCO_3 levels between 75 and 200 mg/l, the pH range for most cultured algal species is between 7 and 9, with the optimum range being 8.2–8.7 [20, 32, 33].

In acidic waters' conditions, only some plants and animals survive. Generally, the younger exemplars of most species are more sensitive to environmental changes. **Figure 4** shows the minimum pH level for different species of fish, shellfish, or the insects which they can tolerate the same amount of acid; for example, frogs can tolerate water that is more acidic (i.e., has a lower pH) than trout [20].

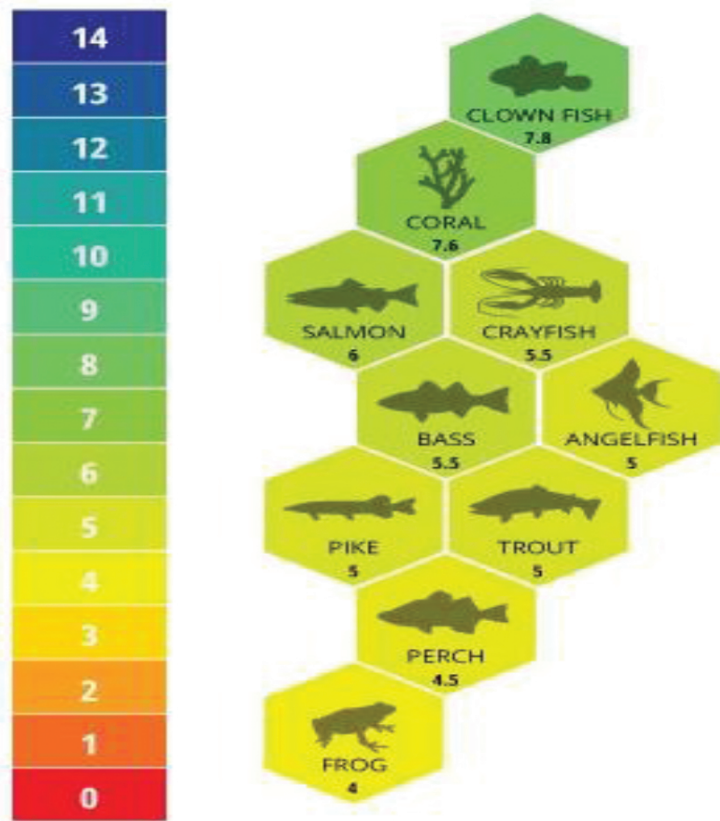


Figure 4. Recommended minimum pH level to survive for different species of aquatic organisms [20, 33].

3.3. Dissolved oxygen

Dissolved oxygen refers to the level of free, noncompound oxygen present in water. Dissolved oxygen concentration is affected by diffusion and aeration, photosynthesis, respiration, and decomposition. The source of the oxygen in the water is the dissolved oxygen from the air and the primary production (photosynthesis process). Depending on the atmospheric conditions, the oxygen enters the water slowly, diffuses quickly by aeration caused by wind, rapid waterfalls, groundwater, etc. The atmospheric temperature and implicit water temperature influence the water oxygen content, and the dissolved oxygen concentrations decrease as temperature increases.

The consumption of oxygen in the lake is the result of two processes: the oxidative and biochemical decomposition processes and respiration (animals, plants, and microbes consume oxygen). The dissolved organic matter is oxidized and the oxygen is taken up by purely chemical oxidation, photochemical oxidation by UV light [25].

Daily and seasonal fluctuations in DO may occur in response to algal and bacterial action. The biological activity increases during the spring, summer, and fall when the photosynthetic activity is high. During the summer and winter, most lakes in the temperate climate are stratified. The combination of thermal stratification and biological activity causes patterns in the water chemistry. The major zones of the lake in relating with oxygen concentration and biological activity are the following [35]:

- The trophogenic zone—the upper stratum of a lake in which photosynthetic production predominates;
- The tropholytic zone—the aphotic deep stratum of a lake where decomposition of organic matter predominates;
- The photic zone—the upper stratum of a lake which receives light input (greater than 1% of surface radiation);
- The aphotic zone—the lower stratum of a lake in which there is no light (less than 1% of surface radiation).

The dissolved concentration varies by season and depth. At turnover (both spring and fall), the O₂ in the water is near 100 % saturation (12–13 mg/l at 4°C at sea level pressure).

During summer stratification, in an oligotrophic lake, the oxygen concentration at depth is influenced by physical processes. The absolute concentration of oxygen decreases in the warmer waters (epilimnion) and increases in the cooler waters (metalimnion and hypolimnion). In a eutrophic lake, the oxygen concentration at depth is influenced by biological processes; the oxidative processes (decomposition and respiration) result in the consumption of oxygen (the dissolved organic matter is oxidized and the oxygen is taken up by purely chemical oxidation, photochemical oxidation by UV light) and the production of oxygen by photosynthesis (primary production):



Circulation (mixing) and primary production in the epilimnion maintain the oxygen at near 100% saturation. Oxidative consumption reduces the oxygen concentrations in the hypolimnion and the oxygen concentrations have less than 100% saturation [35].

Figure 5 shows the variation of temperature and DO with season and depth in lake water. The amount of dissolved oxygen needed varies from creature to creature. Salmon cannot reproduce at a pH levels below 6 mg/l [36]. Coastal fish avoid areas where the DO is below 3.7 mg/l. Bottom feeders, crabs, oysters, and worms need minimal amounts of oxygen (1–6 mg/l), while shallow water fish need higher levels (4–15 mg/l) [37].

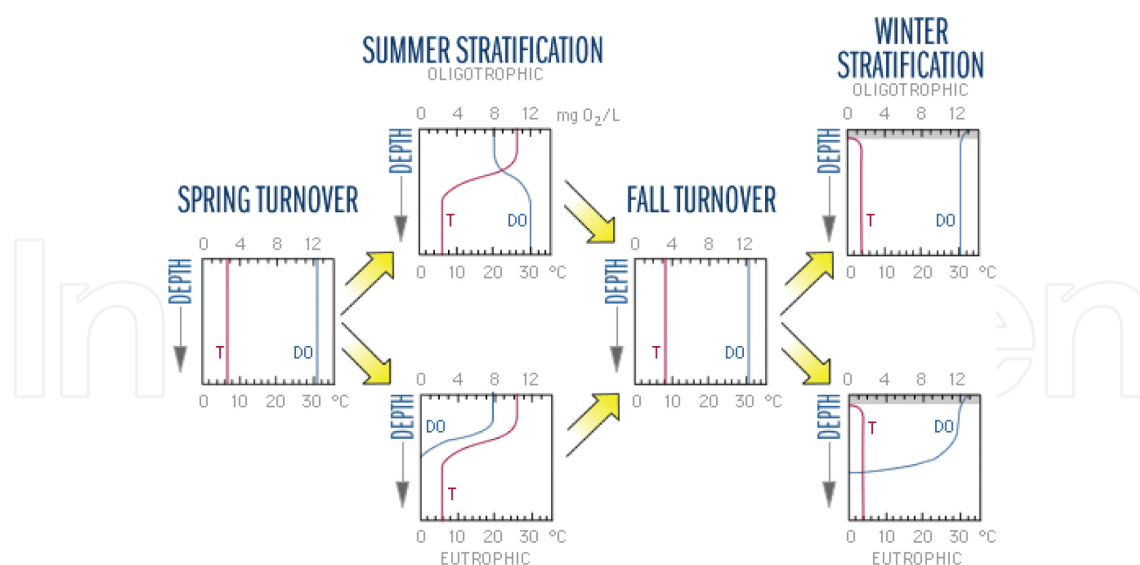


Figure 5. Seasonal fluctuation of temperature and DO with depth [34].

At low concentration of dissolved oxygen, major changes in the types and amounts of aquatic organisms found living in the water can occur. Species such as fish, mayfly nymphs, stonefly nymphs, caddis fly larvae, pike, trout, and bass that need high concentrations of dissolved oxygen will move out or die. They will be replaced by organisms such as sludge worms, blackfly larvae, and leeches which can tolerate lower dissolved oxygen concentrations. Such phenomena usually occur in late summer, when the temperature is high, the DO low, the rate of photosynthesis is intense, and water transparency is low. A fish which is under stress caused by low oxygen levels in the water is more susceptible to poisoning by insecticides or heavy metals, which can be mobilized under reducing conditions [37, 38].

During winter when water is covered by ice the diffusion of oxygen from the atmosphere in the water cannot be realized and fish, plant, and other organism consumption is greater than the oxygen production by photosynthesis. If the frozen water is covered by snow, the light cannot penetrate and photosynthesis also cannot occur. In this circumstance, the microorganisms, fish, plants, and decomposition that consume the oxygen will kill [39].

3.4. Transparency

Secchi depth is the most commonly used method to determine the water transparency (clarity). Water transparency determines the depth of the photic zone and consequently affects the lower limit of light penetration which influences the primary productivity of a lake. Changes in water transparency are determined of suspended sediments: inorganic particulates and colloidal organic matter, humic and fulvic acids, phytoplankton (free-floating algae), and zooplankton. Algae are often the dominant influence on the transparency of lake water [40, 41].

For lakes' trophic state evaluation, the Secchi disc transparency parameter will be associated with another like chlorophyll *a*, and phosphorus concentration [12].

3.5. Nitrogen compounds

Nitrogen is one macronutrient, which is very important for the primary production in the water body. Nitrogen is a dietary requirement for all organisms, because it is a constituent of all proteins and nucleic acids. Plants consist of approximately 7.5% nitrogen (dry mass).

Depending on water properties, various inorganic nitrogen compounds may be found. Nitrogen is mainly present as N_2 , NO_3^- , HNO_2 , NO_2^- , or HNO_3 in aerobic conditions and as N_2O , NH_3 , and NH_4^+ . Ammonium, nitrate, and nitrite have the most important role in biochemical processes. Organic nitrogen includes protein, amino acids, urea, and methylamines [1, 3]. The sum of all quantities of nitrogen contained in organic and inorganic compounds is defined as total nitrogen (TN). Total Kjeldahl nitrogen (TKN) represents the sum of the quantities of nitrogen contained in organic compounds and ammonium nitrogen ($TKN = org-N + NH_4-N$ [mg/l]). For wastewater, Kjeldahl nitrogen is used as a measure.

The main sources of nitrogen in the water are natural and anthropogenic. The discharge of nitrogen is provided by agriculture from the leachate of fertilizers from the agricultural and natural soil, which mainly contain nitrate, ammonia, urea, and amines and various pesticides, industry (pharmaceutical, alimentary, explosives, dyes, fertilizers, etc.), domestic wastewater (detergents, metabolic human products, etc.), food processing, and atmospheric deposition (**Figure 6**) [1, 42].

Nitrogen is a biological inert gas. The excess of N_2 in the water (supersaturations at over 110%) affects several fishes species, causing "gas embolism" or the gas bubble disease.

Ammonia is important as the predominant excretory product of aquatic animals, through the NH_3 excreted directly and also by the degradation of the fecal matter, and uneaten feed. Several types of fishes are affected by ammonia at levels higher than 0.1 mg/l. Carps and tilapias can withstand to concentrations of ammonia higher than 3–4 mg/l.

Nitrite (intermediary between ammonium and nitrate) is only present in smaller quantities in natural waters. The NO_2 combines with hemoglobin and forms methemoglobin, causing the brown coloration of blood, being toxic to fish [44]. The presence of chloride ions and calcium inhibits the nitrite toxicity [45]. NO_2 concentration in hard fresh water pond in fish culture should not exceed 0.1 mg NO_2-N/l , and in seawater, 1.0 mg NO_2-N/l . Nitrate is the major form of nitrogen used by phytoplankton; no toxic effects to fish have been reported at nitrate level below 100 mg NO_3-N/l [47].

Nitrate (NO_3-N) and ammonia (NH_4-N) concentrations are highly variable during the lake seasonal cycles. For deep stratified lakes, nitrate is higher during mixing events and usually decreases in late summer and fall. NH_4-N is generated by heterotrophic bacteria as the primary nitrogenous end product of the organic matter decomposition, and is readily assimilated by plants in the trophogenic zone [35]. NH_4-N concentrations are usually low in oxygenated waters of oligo- to mesotrophic deep lakes because it is nitrified. At lower dissolved oxygen values, nitrification of ammonia ceases and higher amounts of NH_4-N from the sediments are released [48].

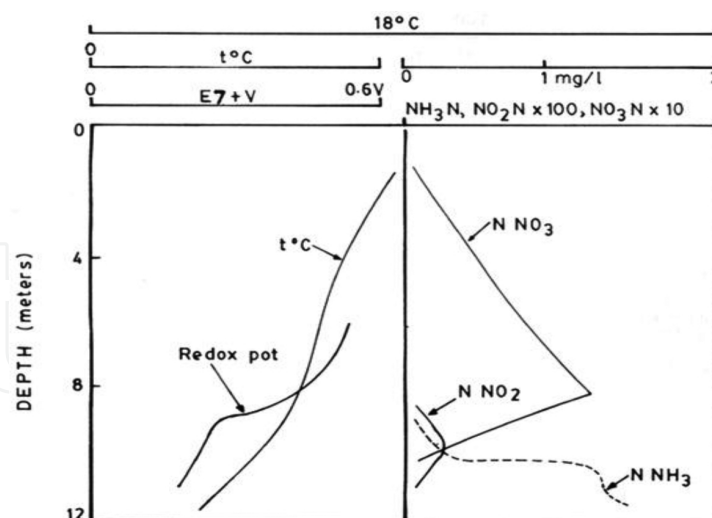


Figure 6. Distribution on depth of the ammonia, nitrate, nitrite, redox potential, and temperature in a temperate lake [43].

3.6. Phosphorus compounds

Phosphorus is one very important macronutrient, which limits the primary production in freshwater. Though phosphorus is the 11th most abundant mineral in the earth's crust, it does not exist in a gaseous state. Phosphorus (P) is an essential nutrient for life, playing a role in the deoxyribonucleic acid (DNA), ribonucleic acid (RNA), adenosine diphosphate (ADP), and adenosine triphosphate (ATP).

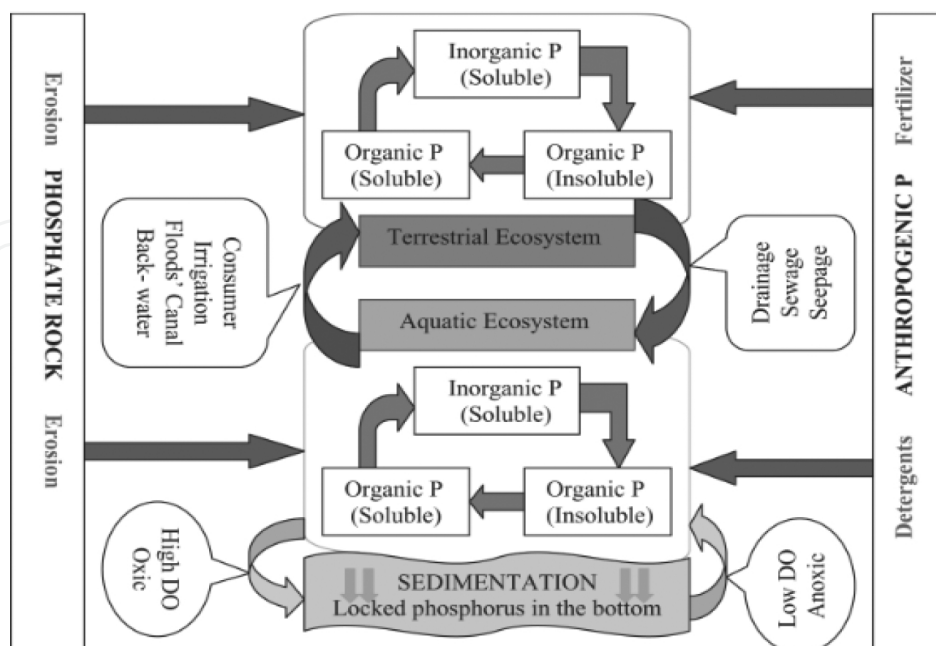


Figure 7. Natural phosphorus cycling between the source, terrestrial, and aquatic ecosystems [6].

The phosphorus in the natural water body is provided by anthropogenic (industrial and agricultural sources) and natural sources. The phosphorus increase is caused by domestic wastewater (detergents and soaps, pesticides, food wastes, and human metabolic waste) [49, 50], food processing industries (meat, vegetable, and cheese processing) [51], distillery, synthetic and natural (cow dung, pig dung, and poultry manure) fertilizers used in agroecosystem [52], agricultural runoff and domestic sewage, phosphate mines [53], and it is very slow, being largely insoluble from mineral matter of rocks (**Figure 7**) [4].

The quantities of phosphorus entering the surface drainage vary with the amount of phosphorus in catchment soils, topography, vegetative cover, quantity and duration of runoff flow, land use, and pollution.

The total phosphorus in aquatic systems, occurs in three forms: inorganic phosphorus (orthophosphate and polyphosphate), particulate organic phosphorus, and dissolved organic phosphorus (soluble and insoluble). The dissolved phase includes inorganic phosphorus, organic phosphorus excreted by organisms, and macromolecular colloidal phosphorus.

Particulate matter includes living and dead plankton, precipitates of phosphorus, phosphorus adsorbed to particulates, and amorphous phosphorus [54]. Total phosphorus concentrations greater than 30 µg/l cause algal blooms in lakes and reservoirs.

Aquatic plants require inorganic phosphate, orthophosphate ions (PO_4^{3-}) for nutrition [55]. This form of phosphate is transferred to consumers and decomposes as organic phosphate soluble and insoluble [35].

The deposition of phosphorus into lake sediments occurs by mechanisms such as:

- a. sedimentation of phosphorus minerals imported from the drainage basin;
- b. adsorption or precipitation of phosphorus with inorganic compounds;
- c. uptake of phosphorus from the water column by algal and other attached microbial communities [56].

3.7. Total nitrogen to total phosphorus ratio, TN/TP (redfield ratio)

Nitrogen and phosphorus are two nutrients, which are necessary for microorganism's growth. The nitrogen can be present in three species: nitrate, nitrite, and ammonia, all species are highly soluble in aquatic environment. If nitrogen is in low concentration, the microorganisms can use the nitrogen from atmosphere; also the nitrogen cannot be limited in aquatic systems. The phosphorus is most important nutrient after nitrogen, its concentration controls the plants growth, and it can be easily uptake by precipitation. The total nitrogen to total phosphorus ratio parameter indicates the stage of plant growth [57, 58].

The ratio of nitrogen:phosphorus 10:1 is ideal for aquatic plant growth, the ratio higher than 10:1 indicates phosphorus limited systems; and nitrate accumulates in abundance in water and the ratio less than 10:1, nitrogen limited systems; nitrate will be used soon as input in the water body [30, 38, 59].

3.8. Chlorophyll *a* (CHL)

Chlorophyll *a* is used as a trophic state indicator. It indicates the ratio between planktonic primary production and algal biomass. The algal biomass generates the main problems resulting from eutrophication. It is easier to measure the value of CHL, the algal biomass. Chlorophyll *a* presents a great variability of the cellular chlorophyll content (0.1–9.7% of fresh algal weight), which is influenced by algal types. Seasonally, a great variability in individual cases can be expected due to composition of species, nutrient availability, and light conditions [3, 61].

3.9. Plankton populations

The general effect of eutrophication on the trophic chain consists of excessive growth phytoplankton and macrophytes vegetation, shift to bloom-forming algal species, which might be toxic or inedible, green or brown coloration of the water, increase in the biomass of benthic and epiphytic algae, change in the species composition of macrophytes vegetation, increase of consumer species biomass, increase of fish killing incidence, reduction in species diversity especially macrophytes, frequent occurrence of low dissolved oxygen events (particularly overnight), large pH changes [6, 14].

The major consequence of eutrophication concerns is oxygen availability. By daylight, photosynthesis phytoplankton produces oxygen and biomass and at night, organisms (animal and plants) and microorganisms by respiration and microorganisms by aerobic decomposing (oxidation) of the dead biomass, consume the oxygen. When the all oxygen will be consumed the oxygen from the sulfate will be used by the anoxic bacteria, will release sulfur which will capture the free oxygen still present in the upper layers and in the deep layer there will be accumulated hydrogen sulfite, which has the smell of rotten eggs.

The changes in the water will lead to important changes in the plankton population. Macroalgae, phytoplankton (diatoms, dinoflagellates, chlorophytes), and cyanobacteria (blue/green algae) will experience excessive growth; some of these organisms can release toxins in the water and be toxic themselves. Gelatinous aggregation that floating on the water surface can be produced by blue-green algae and diatoms. In 1982 and 1983, large amounts of gelatinous aggregations were observed on the Aegean Sea [62].

Macroalgal proliferations, the massive developments in spring and summer, also called green tides, are repeatedly observed in the marine environment. The species implicated are frequently from the genus *Ulva*, *Monostroma*, *Enteromorpha*, *Elodea Myrisphyllus* in fresh waters, *Chaetomorpha*, and *Cladophora*. The increasing amount of these type of macroalgae determine the decreasing amount of much more interesting species for biodiversity (autochthonous long-living) such as *Fucus*. Accumulation of large amounts of these species on beaches can induce numerous nuisances including odor, making it impossible to be used [63].

Most sensitive to oxygen availability, the zooplankton (fish and shellfish, animals with and without limited active locomotion, etc.) may die in oxygen limitation or in water with excessive alkalinity (intense photosynthesis), or toxicity from dangerous metabolic produces (cyanotoxins) or cells themselves of cyanobacteria and other microorganisms.

Humans or animals may be exposed to toxins through the consumption of contaminated drinking water, direct contact with fresh water or the inhalation of aerosols. Toxic compounds can be found free in the water or are cells bound. The normal processes used in treating water for drinking purposes are not efficient so as to remove the free toxins from the water.

Toxins induce damage in animals and humans by acting at the molecular level and consequently affecting cells, tissues, and organs. The main toxin groups include hepatotoxins, neurotoxins, and dermatotoxins, which produce the cyclic peptides, alkaloids, and lipopolysaccharides. The nervous, digestive, respiratory, and cutaneous system may be affected [63].

The symptoms observed on mice using acute doses of hepatotoxins are liver injury and death from liver hemorrhage and cardiac failure within a few hours of exposure. Chronic exposure induces liver injury and promotes the growth of tumors, and cancer. The species of microorganisms that cause the toxic effect are *Microcystis*, *Schizothrix*, *Plectonema*, *Phormidium*, *Lyngbia*, *Cylindrospermopsis raciborskii*, *Anabaena*, *Planktothrix agardhii*, *Aphanizomenon*, *Oscillatoria*, and *Spirula*.

Neurotoxins affect the mice and aquatic birds by causing death in a few minutes through respiration arrest. *Anabaena*, *Oscillatoria*, *Aphanizomenon*, *Lyngbia* are the species responsible for neurotoxins production. Dermatotoxins induce irritant and allergic response in tissues by contact. *Lyngbia*, *Schizothrix*, *Oscillatoria* are most important species which produce the dermatotoxins.

In marine water, over 40 algal species produce the toxins the most important microalgae; *Dinophysis*, *Alexandrium*, *Gymnodinium*, *Prorocentrum*, *Pseudonitzschia* (diatoms) are frequently observed and represent a risk for seafood consumers.

The effects include [63]:

- Amnesic shellfish poisoning (ASP), mental confusion and loss of memory, disorientation, and coma;
- Neurotoxic shellfish poisoning (NSP), muscular paralysis, state of shock, and sometimes death;
- Venerupin shellfish poisoning (VSP). Intoxication leads to gastrointestinal, nervous, hemorrhagic, hepatic symptoms and in extreme cases delirium and hepatic coma.

4. The trophic status assessment

4.1. Simple lake characterizations

Trophic state of a lake can be determined by simply observing its basic characteristics (**Table 1**). More profound approaches of trophic state require analysis of key parameters such as phosphorus, nitrogen, chlorophyll *a*, and Secchi depth [65–68]. **Table 1** shows the trophic state classification based on simple lake characterization [69, 70].

Characteristic	Eutrophic state	
	Oligotrophic	Eutrophic
Total aquatic plant production	Low	High
Number of algae species	Many	Few
Characteristic algae groups	Parse	Abundant
Oxygen in hypolimnion	Present	Absent
Characteristic fish	Deep-dwelling cold water fish such as trout, salmon, and cisco	Surface-dwelling, warm water fish such as pike, perch, and bass; also bottom-dwellers such as catfish and carp
Secchi depth	7.5 m	1.5 m

Table 1. Trophic state classification based on simple lake characteristics [69].

4.2. Trophic state per nutrients, primary productivity and Secchi disc parameters

Ecosystems can be described at different trophic states using grow-limiting nutrients, primary productivity and Secchi disc parameters. **Table 2** shows the average characteristics of lakes, streams, and coastal marine waters of different trophic states.

Water body	Tropic state	TN, mg m ⁻³	TP, mg m ⁻³	CHL, mg m ⁻³	SD, m
Lakes	Oligotrophic	<350	<10	<3.5	>4
	Mesotrophic	350–650	10–30	3.5–9	2–4
	Eutrophic	650–1200	30–100	9–25	1–2
	Hypertrophic	>1200	>100	>25	<1
Streams				Suspended CHL, mg m ⁻³	Benthic CHL, mg m ⁻³
	Oligotrophic	<700	<25	<10	<20
	Mesotrophic	700–1500	25–75	10–30	20–70
	Eutrophic	>1200	>75	>30	>70
Streams				Suspended CHL, mg m ⁻³	SD, m
	Oligotrophic	<260	<10	<1	>6
	Mesotrophic	260–350	10–30	1–3	3–6
	Eutrophic	350–400	30–40	3–5	1.5–3
	Hypertrophic	>400	>40	>5	<1.5

Table 2. Average characteristics of lakes [66], streams [67], and coastal marine waters [68] of different trophic states [13].

To increase the efficiency of a lake management program is used a more sophisticate trophic state index to provide more and complete information about the water state. The characterization of trophic status has been conducted using the following: the Carlson’s trophic state index, the TSI (Carlson’s index).

4.3. Carlson's trophic state index

The trophic state is an absolute scale which describes the biological condition of the water body. The trophic state (TSI) is defined as the total weight of living biological material (*biomass*) in a water body at a specific location and time, a biological response to forcing factors such as nutrient additions [71]. The TSI is the interrelationship between the variables which can be used to identify certain conditions in the lake which are related to the factors limiting the phytoplankton biomass [72]. The effect of nutrients is modified by factors such as season, grazing, mixing depth, etc. For characterizing the trophic state of lakes independent of climate exchange, there were defined the trophic state index (TSI)—Carlson's index Secchi depth, chlorophyll *a*, and total phosphorus; these are three variables which can therefore be used to classify the water body [73]. Three linear regression models are used to calculate the trophic state index and the classified water body: the Secchi disk, TSI(SD); chlorophyll pigments, TSI(CHL); and total phosphorus, TSI(TP). The simplified equation used is presented below [73]:

$$\text{TSI}(\text{SD}) = 60 - 14.41 \ln(\text{SD}) \quad (5)$$

$$\text{TSI}(\text{CHL}) = 9.81 \ln(\text{CHL}) + 30.6 \quad (6)$$

$$\text{TSI}(\text{TP}) = 14.42 \ln(\text{TP}) + 4.15 \quad (7)$$

where TSI(SD) is the trophic state index depending on the Secchi depth, the values of SD is in meters;

TSI(CHL) is the trophic state index depending on the chlorophyll *a* concentration, CHL ($\mu\text{g/l}$); TSI(TP) is the trophic state index depending on the total phosphorus concentration, TP ($\mu\text{g/l}$).

Parameter	Oligotrophic	Mesotrophic	Eutrophic	Hypertrophic
Transparency (Secchi depth), SD, m	>4	2–4	2–0.5	0.5–0.25
Total phosphorus, TP, $\mu\text{g/l}$	<12	12–24	24–96	96–389
Chlorophyll, CHL, $\mu\text{g/l}$	<2.6	2.6–20	20–56	56–155
TSI	30–40	40–50	50–70	>80

Table 3. Assessment criteria for lake Trophic status (SD, TP, CHL, TSI) [9].

More used is the averaging TSI value, which characterizes the central tendency of the trophic state [73–75]. **Table 3** shows the assessment criteria for the lake trophic status regarding the averaging TSI, the Secchi depth, chlorophyll *a*, and total phosphorus concentration [8].

TSI values	Trophic status	Attributes
<30	Oligotrophic	Clear water, oxygen throughout the year in the hypolimnion
30–40	Oligotrophic	A lake will still exhibit oligotrophy, but some shallower lakes will become anoxic during the summer
40–50	Mesotrophic	Water moderately clear, but increasing probability of anoxia during the summer
50–60	Eutrophic	Decreased transparency, warm-water fisheries only
60–70	Eutrophic	Dominance of blue-green algae, algal scum probable, extensive macrophyte problems
70–80	Hypereutrophic	Heavy algal blooms possible throughout the summer
>80	Hypereutrophic	Algal scum, summer fish killing, few macrophytes

Table 4. Carlson’s trophic state index values and classification of lakes [76].

TSI results could be analyzed using Carlson’s scale. This is divided into four steps regarding lake productivity: oligotrophic (least productive), mesotrophic (moderately productive); eutrophic (very productive), and hypereutrophic (extremely productive). In natural condition at largely variation of meteorological parameters, a simple interpretation of trophic state of lake water is not enough.

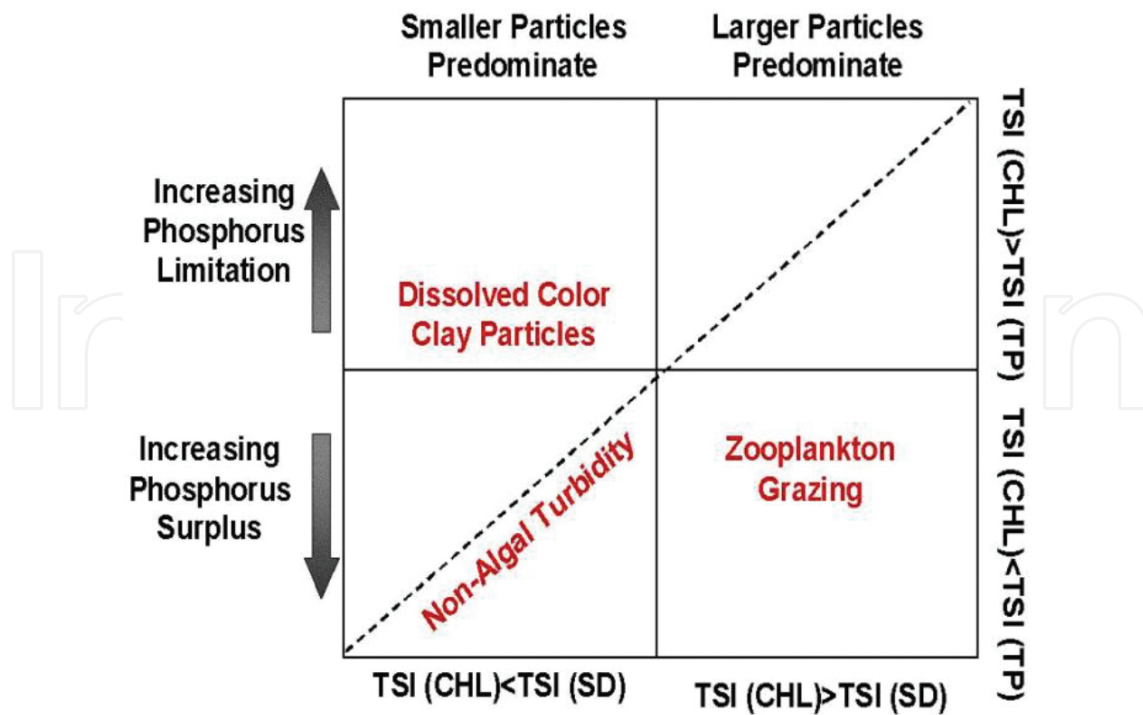


Figure 8. A representation of possible explanations of deviations of the trophic [74].

For complex characterization of natural water must to account of systematic deviations of the simple presentation like in **Table 4**, reported of Carlson in 1992. **Figure 8** illustrates the deviations of TSI(CHL) – TSI(TP) and TSI(CHL) – TSI(SD), and are simultaneously plotted on a single graph, that completes the interpretation of trophic state of natural water. The possibilities are illustrated in **Figure 8** [74]

4.4. Case study: Snagov Lake trophic stage assessment

The Snagov Lake is a natural lake located at 25–30 km North from Bucharest, in Ilfov County, Romania. It is an important natural lagoon on the inferior Ialomita river course with its 5.75 km² surface, 16 km length, and 9 m maximum depth, it is included in national patrimony as natural reservation (**Figure 9**).

The lake water sources are the underground waters and in small part snow and rain waters. As consequence, the water level is relatively constant except in winter and autumn [77].

Samples were collected in 2015 during three annual campaigns: April, July, and October. The duplicate of samples were collected from three sampling points than were chosen to monitor the Snagov Lake: input of Lake-Antena Tancabesti, middle of lake—Complex Pacea and output of lake Santu Floresti (**Figure 9**).

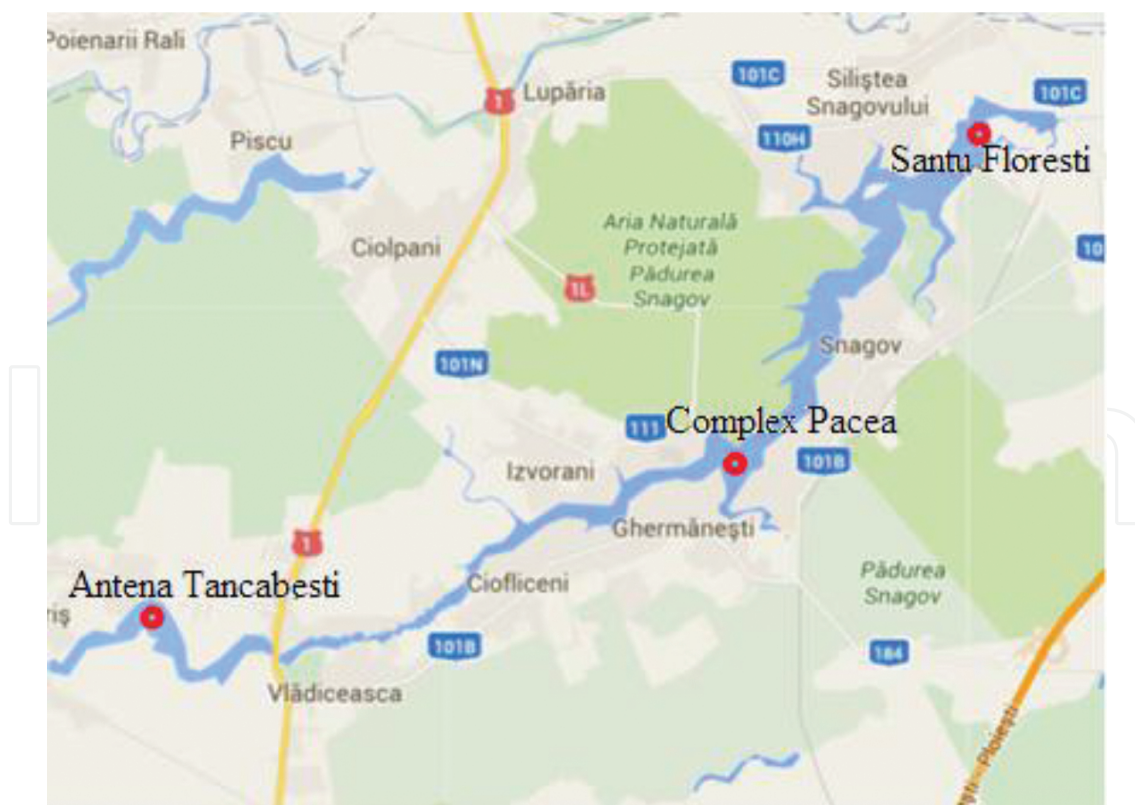


Figure 9. Sampling sites to Snagov Lake: input-Antena Tancabesti, middle-Complex Pacea, and output-Santu Floresti [74].

There were analyzed temperature (T), pH, transparency Secchi depth (SD), total nitrogen (TN), total phosphorus (TP), chlorophyll a (CHL), dissolved oxygen (DO), turbidity (Tr), total suspended matter (Ts) (**Table 5**).

We calculated the trophic state index (Carlson's index), TSI(SD), TSI(CHL), and TSI(TP) using Eqs. (5)–(7) and there average values TSI and using **Figure 7** and **Table 4** the state of lake was characterized. **Table 6** shows the characterization of Snagov Lake in time in sampling points.

Table 6 shows the evolution of water quality of Snagov Lake in time and in space, at input loaded with nutrient in organic and inorganic matter like smaller particles that involve an excessive development of algae and inorganic matter sedimentation in the middle zone of lake until output when the biological activity slowly decreasing and water quality is slightly improvement, all of this in the eutrophic-hypertrophic state of lake. With this evaluation system can identify the status of the lake and can take necessary measures to improve water quality.

Parameter	Input Antena Tancabest			Middle Complex Pacea			Output Santu Floresti		
	Data			Data			Data		
	April	July	October	April	July	October	April	July	October
T , °C	15	29	16	14	28	17	16	29	16
pH	8.4	8.7	7.9	8.3	7.86	7.74	8.5	8.1	7.6
Ts, mg/l,	21.6	32.2	60.8	21.6	19.6	55.2	23.4	40.2	45.2
SD, m	0.5	0.5	0.5	0.8	0.9	0.9	2	0.45	0.9
Tr, NTU	10	51	32	10.9	5.5	11	18	45	8
DO, mg/l	14.8	21.1	16.8	8.7	10.9	9.4	11.0	9.3	11.5
TN, mg/l	1.7	1.99	0.43	1.47	1.41	0.37	1.85	1.9	0.37
TP, mg/l	0.14	0.23	0.09	0.08	0.14	0.05	0.14	0.08	0.06
TN/TP	12	8.7	4.8	18.8	10.1	7.4	13.2	13.8	6.2
CHL, µg/l	2.4	65.2	58.5	3.6	28.4	22.9	2.37	23.5	11.7
TSI(SD)	70	70	70	63.2	61.5	61.5	50	71.5	61.5
TSI(TP)	75.7	82.5	68.2	67.3	75.4	60.6	75.4	67.3	63.2
TSI(CHL)	39	71.6	69.4	43.2	63.4	61.3	53.8	61.6	54.7
TSI	61.6	74.7	69.2	57.9	66.7	61.1	60	66.8	60

Table 5. Average parameter values for Snagov Lake characterization.

Data	Sampling point	TSI	Relation between TSI variables	Eutrophic stage	Attributes
April	Input of lake	61.6	TSI(TP) > TSI(SD) > TSI(CHL)	Eutrophic	Nonalgal and algal turbidity, smaller particles predominate, temperature lower than optimum temperature of algal growth, close to optimal ratio TN/TP
	Middle of lake	57.9	TSI(TP) > TSI(SD) > TSI(CHL)	Eutrophic	Algal and nonalgal turbidity, lower boundary of classical eutrophy decreased transparency, temperature lower than optimum temperature of algal growth
	Output of lake	60	TSI(TP) > TSI(CHL) > TSI(SD)	Eutrophic	Dominance of blue-green algae, algal scum probable, extensive macrophyte problems, temperature lower than optimum temperature of algal growth
July	Input of lake	74.7	TSI(TP) > TSI(CHL) > TSI(SD)	Hypertrophic	Algal bloom, large particulates dominate, light limited productivity, dense algae, and macrophytes, weak nitrogen deficiency, optimum temperature of algal growth
	Middle of lake	66.7	TSI(TP) > TSI(CHL) > TSI(SD)	Eutrophy	Predominant blue green algae, algae turbidity, larger particles predominant, optimum ratio TN/TP, optimum temperature of algal growth
	Output of lake	66.8	TSI(SD) > TSI(TP) > TSI(CHL)	Eutrophic	Algal and non-algal turbidity, smaller particles predominate, slow phosphorus limitation of algal growth, optimum temperature of algal growth, nitrogen limitation
October	Input of lake	69.2	TSI(SD) = TSI(CHL) > TSI(TP)	Eutrophic-Hipereutrophic	Blue-green algae dominate, light attenuation, zooplankton grazing or toxics limit algal biomass, algae death, large particles predominate, nitrogen limitation
	Middle of lake	61.1	TSI(SD) = TSI(CHL) > TSI(TP)	Eutrophic	Dominance of blue-green algae, algal scum probable, extensive macrophyte problems, nitrogen limitation
	Output of lake	60	TSI(TP) > TSI(SD) > TSI(CHL)	Eutrophic	Algal and nonalgal turbidity, smaller particles predominate, nitrogen limit the algae development Temperature lower than optimum temperature of algal growth

Table 6. Values of trophic state index (TSI) (Carlson's index), the state of lake, and characterization of it to input of lake Antena Tâncăbești, middle of Lake Complex Pacea, and output of lake Santu Floresti.

5. Conclusions

Continuous enrichment with nutrients from anthropic sources and enhanced by climate change are important stressors for water bodies. Increasing nutrients concentrations especially nitrogen and phosphorus by anthropogenic sources and extreme weather events, associated with increasing temperature involve important physical, chemical, and biological alterations of water quality. The Carlson's trophic index and its systematic deviations, the TN/TP ratio, and temperature can offer the information regarding trophic state of lake and the characterization of water quality.

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